

TREATMENTS OF HEMI CAUSTIC AND EXTRACTIVES STREAMS

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TREATMENTS OF HEMI CAUSTIC AND EXTRACTIVES STREAMS

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Dedicated to
The Lord of the Universe
JAGANNATHA SWAMI

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LIST OF SYMBOLS AND ABBREVIATIONS

DAF

Dissolved Air Flotation

SUMMARY

Disposal of effluent from pulp and paper industry is one of the major problems faced by entrepreneur in view of increasing environmental standards day by day. In addition to this, industry loses economic value by disposing the effluent or selling it for a low price to other industries. Therefore, to address this problem, in the present study, 2 pulp mill effluents were selected to recover the economic value namely Hemi caustic stream and brown stock filtrate.

As far as the recovery of value of hemi caustic stream is concerned, freeze concentration technique was used to recover water in its pure form and membrane separation was used to separate hemi cellulose from effluent so that permeate can be used as a pure source of caustic elsewhere. In addition to this, hemi caustic stream was subjected to acid hydrolysis to convert hemi cellulose into sugars. These sugars can be used to produce bioethanol.

As far as the recovery of values of brown stock filtrate is concerned, it was proposed to recycle brown stock filtrate as a source of washing water for brown stock washers in the mill. However, continuous recycling of brown stock filtrate into the process causes building up of extractives in the recycle stream which in turn might deposit on the pulp and affects the quality of the pulp. Therefore, it was decided to separate extractives from the brown stock filtrate before recycle it into the mill. Dissolved Air flotation technique was used to achieve the above mentioned objective. An attempt was made to develop an improved and most reliable version of existing extractives measurement method to quantify the performance of Dissolved air flotation technique.

CHAPTER 1

INTRODUCTION

The fast population growth and the augmented demand for industrial establishments to meet daily human life requirements have generated difficulties such as overexploitation of accessible resources, causing land, water and air pollutions. It was said that Pulp and Paper industry as 3rd largest contributor of pollution and 5th largest contributor of the economy of The United States of America. (Nemerow and Dasgupta 1991)

The wood pulping and manufacturing of the paper products create a substantial quantity of pollutants characterized by color, toxicity, suspended solids, chemical oxygen demand and biochemical oxygen demand when untreated effluents are discharged to receiving waters. (Pokhrel and Virarghavan 2004)

The huge amounts of water usage, between 20,000 and 60,000 gallons per ton of product, (Nemerow and Dasgupta 1991) causes large quantities of wastewater generation. The effluents from the industry results color issues, scum formation, thermal impacts, slime growth, and loss of aesthetic beauty of the surrounding environment. Moreover, they raise the quantity of toxic substances in the water, results death to fish and the zooplankton, as well as seriously injuring the terrestrial ecosystem.

The introductions of impurities through waste effluent to various environments can frequently over load the self-cleaning ability of recipient ecosystems. This will result in the buildup of pollutants to problematic levels. An alertness of environmental issues and potential dangers caused by industrial pollutants has impelled several countries to limit

the release of specific toxic substances. The raw pollutants from board, paper and pulp industries can be potentially exceptionally damaging. In fact, a UK industry survey has found that their COD can be as large as 11 000 mg/ℓ (Thompson, Swain et al. 2001). The pollutant amounts in pulp and paper industry effluent is calculated in two important parameters, biochemical oxygen demand (BOD) and total suspended solids (TSS).

Industries are being forced by increasing public awareness of damage caused by these pollutants and strict regulations being imposed by different government authorities to clean their effluents to the standard compliance level before leave them into the environment.

In the above mentioned context, present work focused on treatment of two paper mill effluents namely hemi caustic stream and extractives in brown stock filtrate and it was proposed to treat them in such a way that they could be reutilized in the pulp making process. For instance, after removal of hemi cellulose from hemi caustic stream, it can be used as a fresh source of caustic or it can be sold to other industries. Similarly, after removing extractives from brown stock filtrate which are toxic in nature, it can be used as a fresh source of water for brown stock washers in the mill or it can be disposed into sewer with fewer loads on the mill central treatment system.

CHAPTER 2

LITERATURE SURVEY

2.1 Hemi caustic stream

Hemi caustic stream is one of the spent streams of a typical paper industry that was often disposed without recovering its economic value. Hemi cellulose and caustic soda are the main constituents of hemi caustic stream. Caustic soda is one of the best known pulping materials that can be used in pulping of certain woods to achieve special quality paper. However, it has not been generally used because of its high price and its use will be more expensive in the absence of an efficient and economically feasible recovery method (Claassen, Haar et al. 2000). Therefore, many efforts were made to devise such method by which the use of caustic soda as pulping material could be economically justified. Recovery can be made in two ways. The first way of recovery is to treat the hemi caustic liquor and recycle it into the main process. However, some of the industries may not prefer recycling option because it may compromise the quality of special grade papers. Therefore, this limitation on recycle leads to the second way of recovery into action by separating the caustic from hemi caustic liquor in a pure form using a membrane separation technique. This recovered caustic can be sold to neighbor industries without losing its economic value.

With the first method of recovery, efforts were made to recover the value of hemi caustic liquor by recycling it into the process after applying a suitable treatment method. For example, (Wilson, Beelik et al. 1976) claimed that thermal decomposition of the hemicelluloses present in spent hemi caustic makes these effluents appropriate for use in

refining, bleaching and cooking of dissolving pulps without ill effect on pulp quality. They also claim that thermal treatment of spent hemi caustic makes the dissolved hemi cellulose safe and significantly remove deposition of the hemi celluloses on cellulosic materials when these effluents are utilized. Similarly, (Partlow and Wash 1965) claimed that the controlled oxidation of dilute spent alkaline refining solutions containing only some 3 to 15% of sodium hydroxide and contaminated with organic matter makes it possible to reuse the solution. Moreover, (Barton, Schoeffel et al. 1954) claimed that they invented a soda method of producing pulp from wood, and is more particularly concerned with such a process which allows the practical regeneration of soda, with substantially no loss in washings and stack gases, elimination of the necessity of smelting, the hazards of glowing soda ash and affords a practical method of recovering soda cooking liquor from waste liquors containing the same. However, no efforts were found in the literature related to the second method of recovery; separation of caustic from spent liquor in its pure form. Therefore, a study of the second method mentioned above was proposed.

The major constituent of this hemi caustic stream is water. Evaporation has been a traditional approach to remove water. However, evaporation leaves the caustic and remaining constituents in the form of sludge which is quite complicated to separate. Moreover, evaporation is not an energy efficient operation as water is lost to the environment. Hence, the method of freeze concentration was proposed not only to recover the caustic in its pure form, but also water in the form of ice crystals. We are anticipating there will be a shift in the equilibrium at low temperature, so either the sodium ions or the remaining constituents will be transferred to water. Therefore, the separation of caustic from hemi caustic extract would be accomplished.

Another way of recovering the value of hemi caustic is by hydrolyzing the hemi cellulose into sugars and converts them into bioethanol through regular fermentation process. Freeze concentration as a previous step to the acid hydrolysis certainly increases the concentration of hemi celluloses in the mother liquor and thereby increases the production of bioethanol. The present work was mainly focused on investigating the possibility of recovering either hemis or caustic in the form of value added products.

The effect of two pretreatment methods were studied namely heat treatment, freeze concentration before subjecting hemi caustic liquor to membrane separation. Heat treatment may not be a feasible method in the present case as applying heat breaks long chain hemi cellulose molecules into smaller molecules and escape through the membrane and ruin the whole purpose of separating out hemi cellulose from hemi caustic in the pursuit of recovering caustic. Otherwise, high rates of throughputs were observed because of the reduction in viscosity of the solution. Therefore, freeze concentration method was proposed. Applying freeze concentration will remove water and reduce the load on the membrane and in turn enhances the life of the membrane. Unlike evaporation which consumes more energy than the freeze concentration, water could be recovered and reused in the mill. This recovery process requires washing of hemi caustic mother liquor from the ice crystals and this washing operation freezes the washing water after some period of time when washing water temperatures reaches the ice crystal temperature. To alleviate this problem of freeze concentration, possibility of application of gas hydrate technology was discussed.

2.1.1 Membrane separation

Reducing the water consumption in paper mills by purifying and recycling mill effluents using membrane filtration has been studied in many investigations. A number of commercial installations are also in operation. Use of membrane separation techniques in pulp and paper industry is known since last 15 years. A great deal of effort has been put into purification of pulp and paper waste effluents using membrane technology to meet the ultimate goal of running mill at closed loop condition. For example, (Nataraj, Sridhar et al. 2007) developed a membrane based microfiltration/electro dialysis hybrid process for the treatment of paper industry waste water. (Pizzichin, Russo et al. 2005) worked on purification of pulp and paper waste water with membrane technology for water reuse in a closed loop. (Liu, Liu et al. 2004) explored the treatability of Kraft spent liquor by microfiltration and ultrafiltration. In addition to this, (Liu, Liu et al. 2004) explored the application of inorganic membranes in the alkali recovery process. (Wallberg, Jonsson et al. 2003) worked on fractionation and concentration of Kraft black liquor lignin with ultrafiltration. (Maartens, Jacobs et al. 2002) studied the fouling prevention and cleaning methodologies of ultra-filtration of pulp and paper effluent. (Jokinen and Nystrom 1996) compared membrane separation processes in the internal purification of paper mill water. (Nystrom, Kaipia et al. 1995) worked on fouling and retention of nano filtration membranes. (M. D. Afonso and De Pinho M. N. 1991) explored different membrane separation processes in the pulp and paper industry. (Bindoff, Davis et al. 1987) worked on the Nano filtration and reuse of effluent from the caustic extraction stage of wood pulping.

2.2 Extractives in the Brown Stock Filtrate

Since last few decades, the pulp and paper industry has been faced with strict limitations on its discharge effluents and it is expected that the similar trend will continue in the future. In addition to this, the rising demand to decrease water consumption has forced pulp mills to develop some more competent methods for pulp washing. The circulation movement of filtrates has augmented and internal water treatment is been in use nowadays. Water shortage is already a big problem in several countries.

Regardless of the huge process investments in environmental fortification, the auxiliary waste water treatment will become ever-more important in the future because of huge quantities of generated wastewater. (Leiviska 2009)

Brown stock filtrate from Rayonier Performance fibers mill, Jesup, Georgia was selected for the present study with an objective to treat and able to recycle it into the process. Brown stock filtrate contains wood extractives and it needs pretreatment for the following reasons.

2.2.1 Ill effects of wood extractives

Brown stock filtrate consists of wood extractives and these extractives can cause lethal and hormonal consequences in aquatic surroundings at extremely low concentrations(Oikari, Lönn et al. 1983). Biological treatment eliminates most of the wood extractives (Kostamo and Kukkonen 2003). However, wood extractives can be altered to other toxic compounds when they are subjected to biological treatment. Moreover, there is no proper guarantee that biological treatment work intact always, and grave toxicity problems may seldom occur.

Apart from being lethal to aquatic life, wood extractives causes production issues as well in the pulp and paper mills, for instance, pitch settlement on process equipment and pulp quality issues. Rigorous water recirculation in pulp and paper industry generates wood extractives buildup in the water cycles.

The competent elimination of challenging elements from process waters will enable to shut down the water circuits. Moreover, this would reduce quantity of wastewater generation. Supplemental treatment of polluted water reduces the amount of harmful substances and their entree to the main water system. In addition to this, pretreatment prior to biological wastewater treatment will have a constructive impact on the performance of the biological treatment process.

2.3 Objective

The purpose of the present study is to investigate the effectiveness of ways and means by which the economic value of pulp mill effluents such as hemi caustic stream and brown stock filtrate could be recovered. A major portion of the study is concentrated on developing treatment systems for the above mentioned pulp mill effluents. In addition to this, an effort was made to develop robust analytical methods for the measurement of extractives and hemi cellulose which was critical to assess the performance of treatment systems developed in the lab.

CHAPTER 3

EXPERIMENTS

3.1 Hemi caustic stream

3.1.1 Experimental section

Recovery of caustic from hemi caustic stream involves two steps. The first step deals with the separation and recovery of water from hemi caustic using freeze concentration technique. The second step deals with the separation of sodium ion from concentrated hemi caustic extract using any physical separation technique such as membrane separation.

3.1.1.1 Freeze concentration

Two experimental setups were used. The first setup was shown in Figure 3.1.

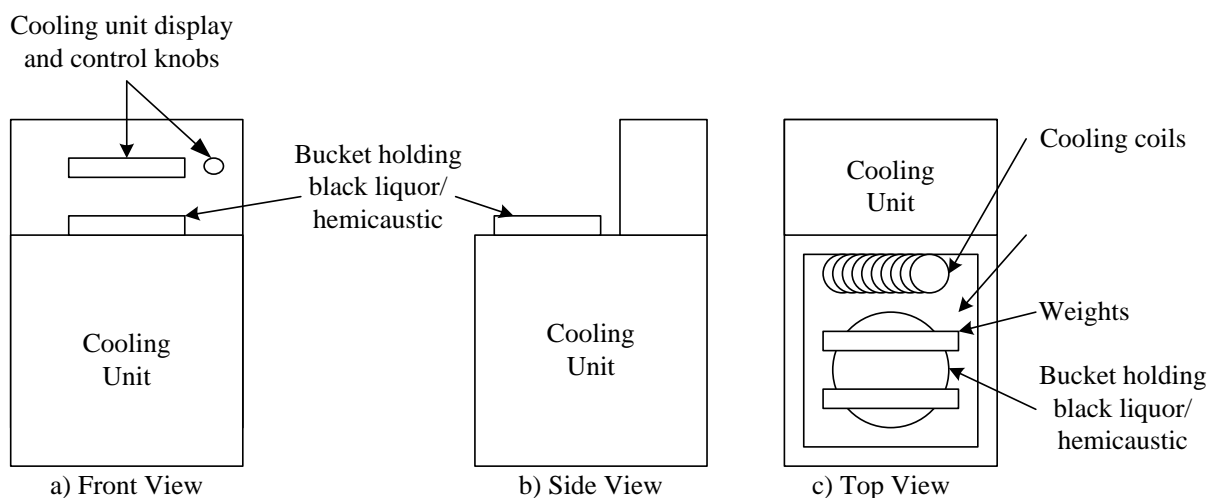


Figure 3.1 The first experimental apparatus showing the (a) front view, (b) side view, and (c) the top view.

The first experimental setup was used in the beginning of the investigation for freeze concentration of hemi caustic stream. A metal bucket (actually, 1 L pressurized vessel) containing hemi caustic stream was lowered into the cooling unit tank, which held coolant (antifreeze). The coolant was cooled to about -20°C . Due to experimental difficulty, the coolant temperature was not able to be controlled with the cooling unit. After a couple of experiments, super cooling then over-freezing was a huge problem in the experiment, so a second experimental setup was adopted which was shown in Figure 3.2: one that could stir the solution and minimize super cooling and rapid freezing.

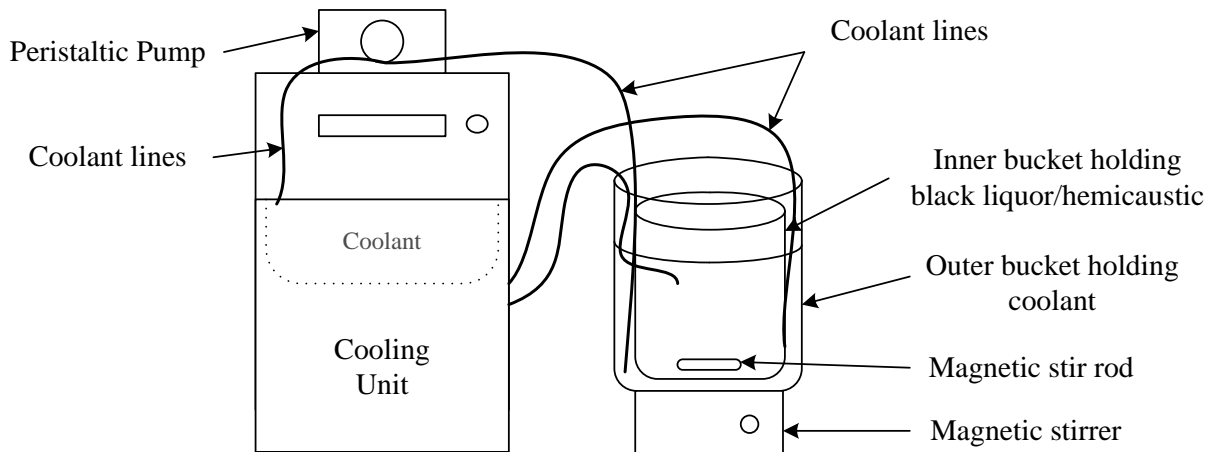


Figure 3.2 The second experimental apparatus with magnetic stirrer

The second experimental setup uses a magnetic stirrer and stir rod. Coolant was circulated around a plastic bucket holding the hemi caustic stream. The plastic bucket had smooth walls, which reduced the number of nucleation sites compared to the metal

vessel (which had rough sides). A peristaltic pump was used to increase the flow of coolant around the inner bucket, increasing the flow rate of coolant.

However, second experimental setup also posed problems such as inefficiency of mixing and under cooling because of heat gain by the refrigerant from the atmosphere when it was being circulated through the plastic bucket. Therefore, second experimental setup was modified as shown in figure 3.3 by replacing the magnetic stirrer with a mechanical agitator and by directly placing the container in the middle of the coolant.



Figure 3.3 The modified second experimental setup with agitator

3.1.1.2 Experimental Procedure

Throughout the course of this experiment, the experimental procedure was changed and fine-tuned, but for the most part, the idea remains the same. Hemi caustic stream was cooled to freeze the water in the solution. The ice was then removed, weighed, and then the total dissolved solids were found for the remaining mother liquor and the collected ice.

The amount of dissolved solids (TDS) was always found in the same manner. About 10 mL of sample was transferred to a pre-weighed aluminum tray. The mass of

the solution and tray was then found. The tray with the solution was placed in a 100°C oven for one to seven days. After one to seven days, the mass of the dry sample tray was found. Subtracting the mass of the dry sample and tray from the mass of the wet sample and tray gave the amount of water evaporated. The mass of the dry sample and tray minus the mass of only the tray gave the mass of the dissolved solid within the sample solution. Finally, the percentage of dissolved solids in the sample solution could be found. Before hemi caustic stream was concentrated using freeze concentration, experiments were conducted with black liquor to setup an experimental apparatus and develop a procedure. The experimental setup initially used is displayed Figure 3. After over freezing of the black liquor, the setup displayed in Figure 4 was adopted. After successfully collecting ice at several intervals, the sample solution was changed from black liquor to hemi caustic stream.

After many runs, and many changes to previous procedure, the final procedure was proven to be successful. The coolant temperature around the bucket holding the hemi caustic stream was not able to get cold enough to form ice in the hemi caustic stream; therefore, the following procedure uses the experimental setup displayed in Figure 3.

- 1) Turn on the cooling unit. Be sure to keep the cooling unit's circulation tubes submerged in the coolant in the cooling unit.
- 2) Once the coolant temperature reaches about -10°C, turn off the cooling unit. If the coolant warms up to about -7.5°C, turn the cooling unit back on. The coolant temperature should be kept in the range of $-10 \pm 2.5^\circ\text{C}$ to avoid supercooling the sample (which leads to rapid ice crystal formation once a nucleation site is

introduced) and to ensure the sample freezes (the freezing point is around -4.5°C to -4.7°C).

- 3) Next, transfer 500 mL of hemi caustic stream to a 1 L plastic bucket.
- 4) Place the plastic bucket into coolant pool in the cooling unit.
- 5) Add a couple weights to the top of the bucket to ensure the bucket does not float and then flip over.
- 6) Find the total dissolved solids (TDS) of the mother liquor.
- 7) Monitor the temperature of both the coolant and the hemi caustic stream.
- 8) Once the hemi caustic stream temperature reaches 0°C , start a timer or write the time down.
- 9) Occasionally stir the hemi caustic stream solution and scrape the sides of the bucket.
- 10) Once the solution reaches a temperature of about -4.7°C , be sure to scrape the sides of the bucket about once a minute until ice has formed.
- 11) About 30-45 minutes after the temperature of the hemi caustic stream had reached 0°C , a fair amount of ice (40-100 g) should have formed
- 12) Collect the ice with ice collection tool displayed in Figure X. Allow all the liquid to flow through the ice and screen and back into the 1 L bucket.
- 13) Be sure that some ice crystals remain in the remaining mother liquor (hemi caustic stream). These will act as nucleation sites for future ice crystal growth.
- 14) Transfer the ice into a pre-weighed beaker and find the mass of the collected ice.
- 15) Immediately find the TDS of the remaining mother liquor.
- 16) After the ice has melted, find the TDS of the collected ice.

- 17) Continue freezing the hemi caustic stream mother liquor for about 30-45 minutes.
- 18) Collect the ice after a reasonable amount of ice has formed.
- 19) Repeat steps 12-18 for each successive collection of ice.

3.1.1.3 Membrane Separation

Schematic diagram of experimental setup for membrane separation operation was shown in Figures 3.4 and 3.5. This setup mainly consists of locally designed stainless steel test cell, and a nitrogen gas cylinder facility for pressurizing the hemi caustic liquor. A stainless steel membrane support was designed and placed below the membrane to protect the same from shape deformation caused due to high pressures. Many trails were conducted and finally a successful trail was achieved by pressurizing the liquid through the membrane without any leak. Water was used for preliminary trails and then original hemi caustic solution was used from the leak free trail onwards. Trails were conducted to determine the operating pressure range for the current experimental setup. In an industrial point of view, high pressures are favorable because they give better flow rate and less processing time. Hence, high pressures such as 300psi and 400psi were applied to determine the optimum high pressure at which membrane could be operated without deformation and leaks. It was observed that for the current experimental setup, 200psi is the highest pressure at which solution could be pressurized through the membrane without any leak and with minimum deformation of the support. Trails were conducted at 100psi, 150psi and 200psi. Filtrates were collected for the analysis of hemi cellulose content. Membranes after subjecting to 100psi and 200psi can be seen in pictures below. In addition to this, filtrates collected at different pressures can be seen in Figure 3.10.

Membrane support before and after subjecting it to nitrogen gas pressure was shown in Figures 3.6 and 3.7 respectively. All the separation experiments were conducted at room temperature. During every batch experiment, 200 grams of feed solution were introduced to the test cell, and 15 to 20 grams of permeate were collected.

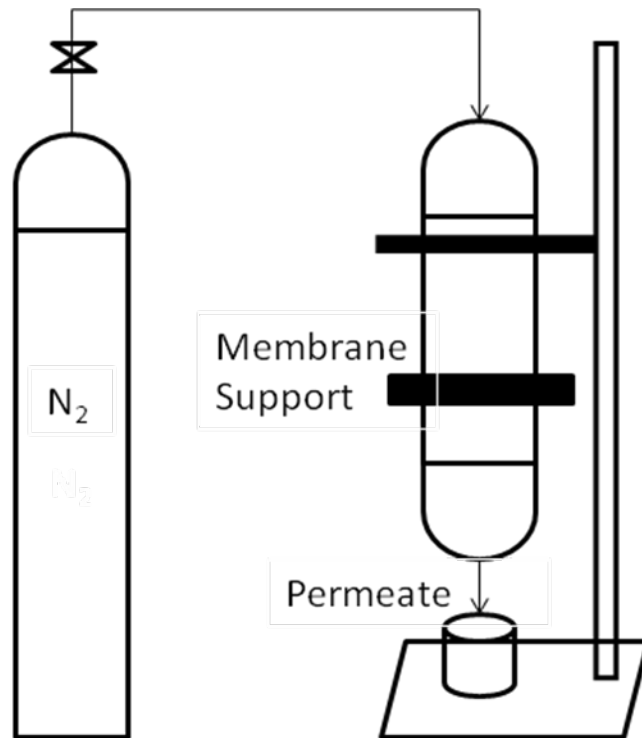


Figure 3.4 Schematic diagram of Membrane separator



Figure 3.5 Membrane separator



Figure 3.6 Membrane support before subjected to nitrogen gas pressure

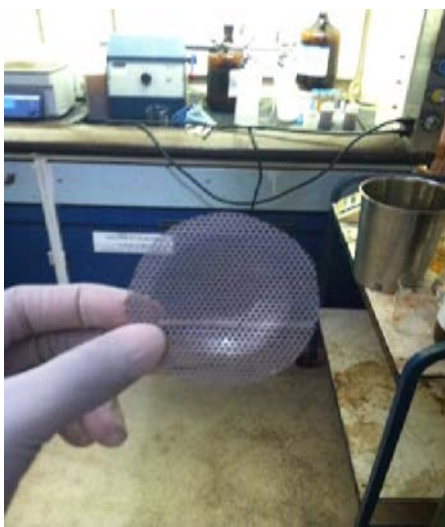


Figure 3.7 Membrane support after subjected to nitrogen gas pressure



Figure 3.8 Membranes after subjecting to 100psi pressure (One side, the other side)



Figure 3.9 Membranes after subjecting to 200psi pressure (One side, the other side)

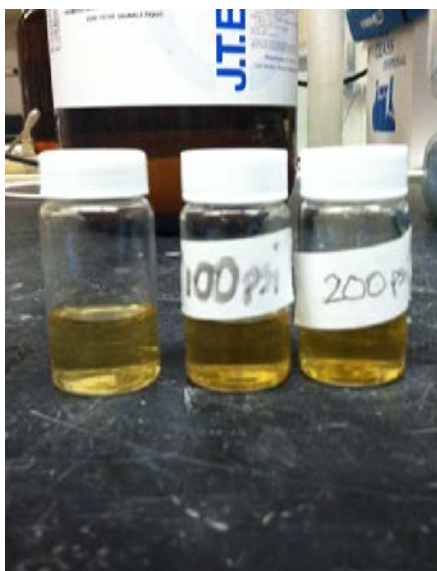


Figure 3.10 Feed sample, Filtrate at 100 psi and Filtrate at 200psi

3.1.2 Analytical section

3.1.2.1 Acid hydrolysis

Acid hydrolysis converts hemi cellulose into sugars and by measuring the sugars formed, one can measure the hemi cellulose indirectly. However, this method works based on the assumption that acid do not eat hemi cellulose in the sample.

To conduct the acid hydrolysis, hemi caustic sample (10-20 mL) was placed into a beaker, sulfuric acid (95%) was transferred to a small graduated cylinder, and the following equipment was used: a pH meter, High Performance Liquid Chromatographer, litmus paper, 25 mL long necked Erlenmeyer flasks. A small dropper was used to transfer sulfuric acid from the graduated cylinder into the hemi caustic sample. A note of the volume of acid used for each sample was taken. After each addition of approximately 3-5 drops of acid, the pH of the hemi caustic sample was tested with litmus paper until the p^H was below 10 so the pH meter would not get damaged. Below 10, the pH meter was used to measure the P^H . Around a pH of 3, the number of acid drops was reduced to 1-2

drops between P^H readings so the desired P^H was not passed. Once the desired P^H (1-2) was reached, the sample now had a bright white color from the salt precipitate, and was transferred into a 25mL long necked Erlenmeyer flask with a loose covering. The sample was then transferred to a pressurized autoclave for one hour at 120° C. After the sample was allowed to cool in the autoclave, the HPLC was used to analyze the sample for sugars (glucose, xylose, galactose, arabinose, and mannose).

3.1.2.2 Measurement of caustic

It was decided to measure the concentration of the caustic of both the feed and permeate from membrane separation operation to make sure that membrane is not withholding the caustic as the recovery of caustic is main purpose of membrane separation operation. Sodium hydroxide concentration was measured by titration with 0.5N sulfuric acid to P^H 8.2.

3.2 Treatment of Extractives in Brown Stock Filtrate

3.2.1 Experimental section

A 2 liter batch reactor to saturate brown stock filtrate with air (110psi) and a custom column set up (Figure 3.11) was used to represent the DAF for laboratory scale tests. Schematic diagram of dissolved air flotation set up and column dimensions were shown in Figures 3.12 and 3.13 respectively.



Figure 3.11: Dissolved Air Flotation setup

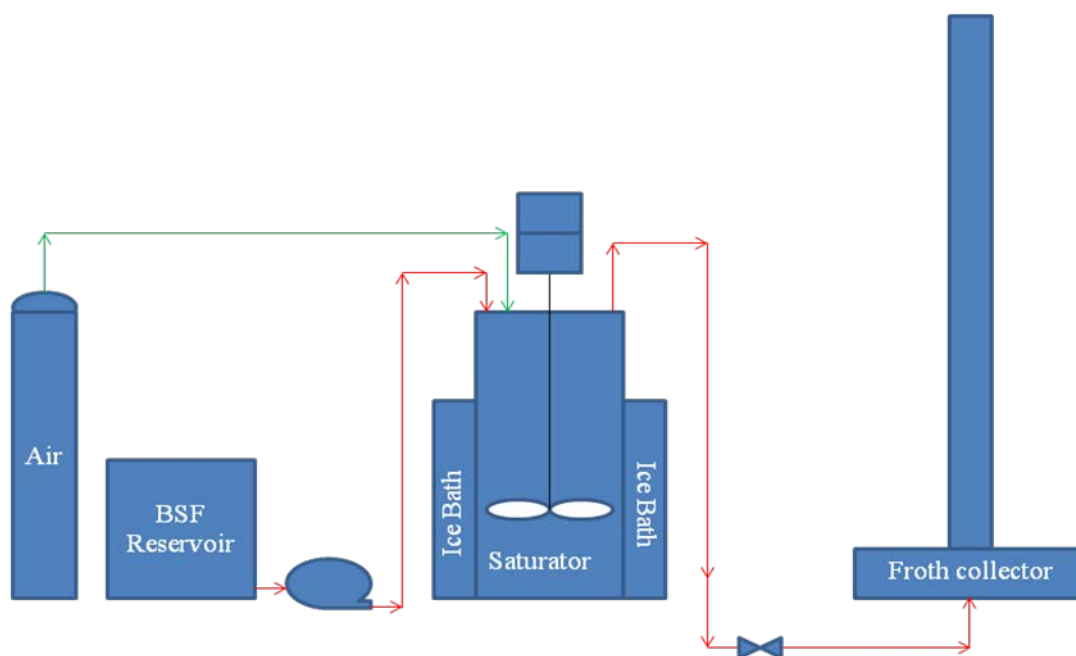


Figure 3.12: Schematic Diagram of Dissolved Air Flotation setup

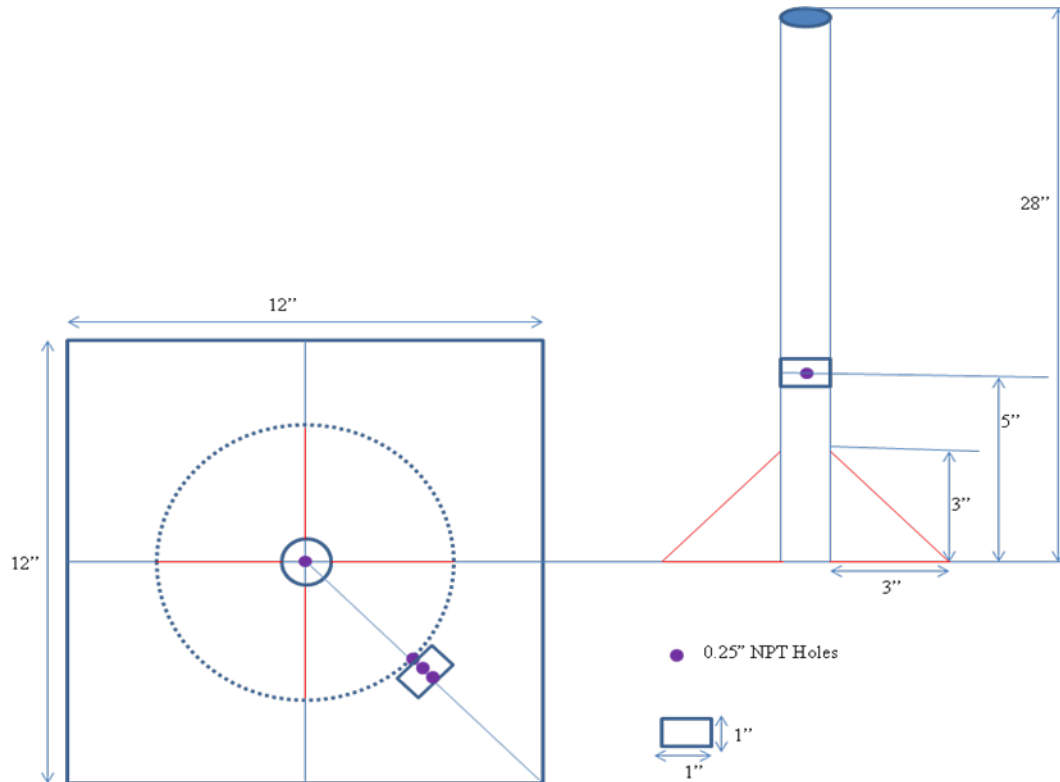


Figure 3.13: Dissolved Air Flotation Column dimensions

The solution is first weighed on a scale with a tare function to obtain 1350-1500g of the brown stock. Then exactly 150 ml of polymer measured out, or none if the batch requires no polymer. This is then charged into the saturator using a peristaltic pump; during this process the mixture was well mixed, to ensure that the fines do not clog the hose of the pump. For the acidic conditions, sulfuric acid was used to reduce the pH of the brown stock filtrate and a pH meter to measure the over-all concentration. All stock concentrations were within 3.46-3.5 pH, treated the acidic stock in the same manner as the basic stock in terms of charging it into the column.

Once the reactor is charged, ice is placed into the basin around the reactor base to help cool down the vessel, and increase the amount of air that will dissolve into the solution. The ice will remain for a few hours. Once the ice has melted, the basin was

emptied then refilled with ice. Then the hoses are moved, and the entry point where the sample enters is closed, and the air hose is hooked up, and tightened. The high-shear mixer is turned on to provide agitation and the timer is started.

30 minutes to one hour residence time is allowed depending on the test. Once the solution is ready, it will be released from the reactor, and the air shut off. The pressure of the air inside the vessel should be enough to push the solution from the reactor, into the column. This may not always be the case, so a little air should be allowed to help the sample out of the reactor and into the column.

Once the solution is released in the column, extractives attached to the bubbles rose up to the surface. After 10min, a sample of the supernatant was taken and subjected to extractives analysis procedure. Fines collected on the surface of brown stock filtrate inside the column and column after dissolved air flotation operation were shown in Figures 3.14 and 3.15 respectively.

For fines measurement, a metal tray is first weighed and the weight recorded, then a small amount of sample is added, and once again weighed. This is then placed in the drying oven to remove the liquid and leave nothing but the solids. The dried tray is then weighed, and the percentage of the sample that is solids is determined. This value is then compared with the value obtained by repeating this procedure with the feed stock to determine the amount of fines removed.

The color of the collected sample was determined by taking 1 ml of sample, and combining it with 9 ml of 7 pH buffer solution. This is then filtered through 0.7 μm filter paper to reduce turbidity. Then the absorbance of the diluted sample is measured at 465 nm. This gives us absorbance reading that we can compare to feed stock solutions.



Figure 3.14: Fines collected on the surface of brown stock filtrate inside the column

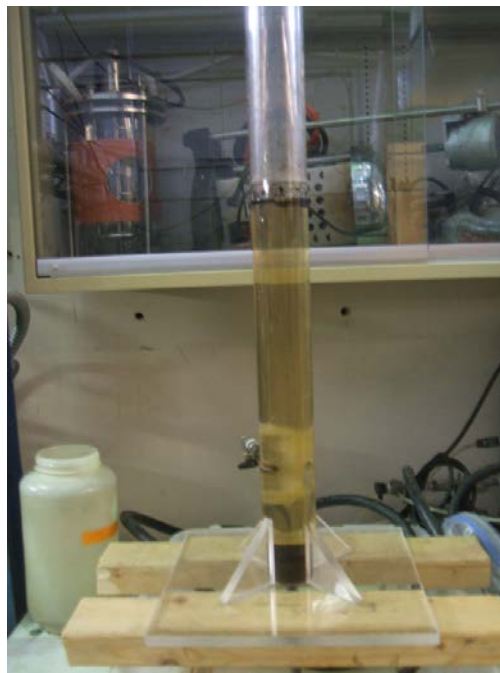


Figure 3.15: Column after dissolved air flotation operation

3.2.2 Analytical section

3.2.2.1 Extractives measurement (Indirect method)

The method was termed as indirect because it cannot give the independent amounts of extractives present in the brown stock filtrate. In addition to this, it is a manual method and the result heavily influenced by the doer of the analysis and many other factors that were discussed elsewhere. The following procedure was used to assess the extractives.

1. Shake the sample bottle vigorously.
2. Filter the sample with a Buchner funnel and Whattman filter paper. (Solids tend to be entrapped in glass fiber filter media, and are difficult to separate from the filter media)
 - a) Use a clean 1L Erlenmyer flask to receive the aliquot.
 - b) Use the house vacuum to facilitate the filtration.
 - c) Measure approximately 50 g (V) of the aliquot and transfer the volume to a 1L separation funnel.
3. Add 200ml dichloromethane into the 1L separation funnel.
4. Shake the mixture vigorously for 10 second.
5. Open the valve on the separation funnel and vent the vapor pressure inside.
6. Close the valve and shake separation funnel vigorously for another 10 second.
7. Repeat steps 4 and 5 until there is no pressure build-up inside the separation funnel.
8. Shake the separation funnel for another 60 seconds.
9. Settle the aliquot in the separation funnel for 10 min.

10. Collect the lower portion of the mixture (dichloromethane and water suspension phase) and if
 - a. If yellowish floating phase (water) on the top of the collection was observed, proceed to steps 11 through 13
 - b. Otherwise proceed to step 14.
11. Transfer the filtered aliquot to another 500ml separation funnel.
12. Collect the clear and transparent dichloromethane phase on the lower part into a 250ml round bottom flask.
13. Discard the yellowish tan color top layer liquid.
14. Use Buchi Rotavapor to reduce the dichloromethane to around 10ml.
15. Transfer the 10ml dichloromethane to a pre-weighed scintillation vial (W1).
16. Dry the scintillation vial in the oven at 105°C for 1 hour.
17. Cool the scintillation vial in a desiccator to room temperature and weigh the scintillation vial again (W2).
18. Calculate the extractives concentration: $c = \frac{W2 - W1}{V}$ (g/L)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Hemi caustic stream

4.1.1 Freeze Concentration

It was decided to ensure the reliability of freeze concentration in terms of concentrating mother liquor before subjecting the samples to membrane separation. Therefore, freeze concentration experiment was conducted. Ice and mother liquor were collected at different time intervals for the analysis of total dissolved solids. Collection time was taken as 0 minute when cooling operation of hemi caustic solution was started. Because of this, total dissolved solids at 0 minute was shown in Fig 4.1 only for mother liquor as mother liquor was at room temperature and ice was not formed yet. In addition to this, total dissolved solids content of both ice and mother liquor was shown for 40 minutes. Fig 4.1 shows the total dissolved solids of the collected ice and the remaining hemicaustic (mother liquor) vs. time. The collected ice is not pure water: some solid from mother liquor is still trapped within the ice. Moreover, some amount of solid was attached to the walls of the ice. An attempt was made to wash these walls. However, quick melting problem was faced. Therefore, washing operation was abandoned. But, a separation was apparent, such as recrystallization, distillation, evaporation, extraction and absorption. As time continues, the solid concentrations in the mother liquor an increase which was an expected trend. As a matter of fact, we should see zero percent total dissolved solids in ice. However, ice was not washed because of the quick melting problem. Therefore, the contribution of the solids from the external and internal parts of

the ice contributed the total dissolved solid content almost similar to mother liquor at 40minutes.

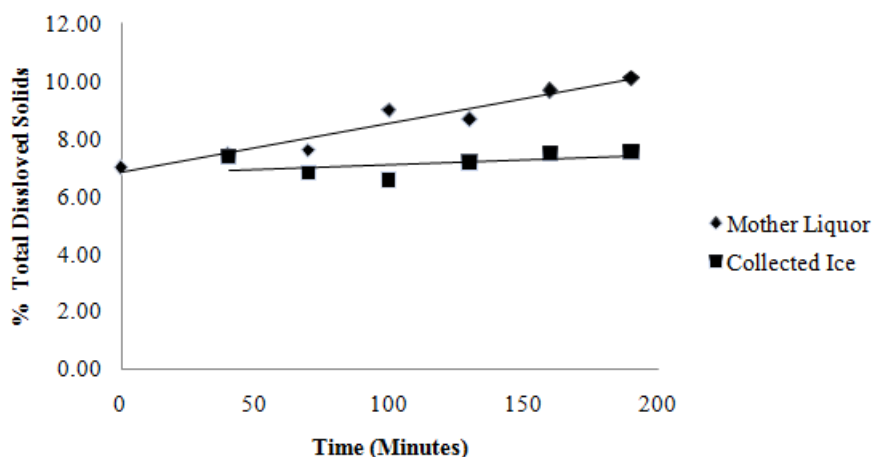


Fig. 4.1 Variation of % Total dissolved solids with freezing time

(Data for all plots shown in Results & Discussion chapter was presented in Appendix A)

Later, hemi cellulose contents of hemi caustic at different pH values was measured to understand the effect of the presence of caustic on the hemi cellulose content of hemi caustic. Due to the presence of hemi cellulose in the caustic effluent, acid hydrolysis should produce sugars; however, the caustic present in the effluent could degrade the hemi cellulose rendering sugar production impossible. After HPLC analysis, sugars were found in all the samples hydrolyzed thus the caustic does not destroy all the hemi cellulose. Table 4.1 shows the results of the HPLC analysis for all samples prepared.

Table 4.1: Sugar contents of samples at different pH values (g/L)

Sample	1	2	3	4
pH	0.98	1.01	1.97	1 ^a
Glucose	0.0	0.0	0.0	0.0
Xylose	2.2	1.79	0.45	2.48
Galactose	0.0	0.16	0.0	0.0
Arabinose	0.0	0.0	0.09	0
Mannose	0.0	0.0	0.0	0.0
Cellulose	0.0	0.0	0.0	0.0

^a With freeze concentration

Samples 1, 2 and 3 were samples of hemi-caustic subjected to different pH conditions. Sample 4 was a sample of hemi-caustic collected at the end of freeze concentration stage. As is evident in the table 4.1, as the pH increases, the total concentration of sugars decreases. This result is expected as hemicellulose is a polysaccharide composed of the mono saccharides, and as the pH decreases, the acid breaks more hemicellulose chains increasing the concentration of mono saccharides. In sample 4, the concentration of sugars (xylose) is higher than the other samples prepared at a similar pH. This result supports the findings in the freeze concentration experiment because the higher sugar concentration indicates a higher concentration of hemicellulose. Xylose is the most common monosaccharide found in hemicellulose chains, and the results support the same.

4.1.2 Membrane Separation

The primary objective in this section of the study is to develop methods those could enhance the life of the membrane. The secondary objective is recovery of caustic from hemi caustic by separating out hemi cellulose using membrane separation. Caustic concentration of feed and filtrate for 100psi pressure experiment were measured to determine the efficiency of the membrane in terms of its ability to pass the caustic through it.

It was observed that 70.4% of caustic could pass through the membrane. Caustic concentration results were shown in Table 4.2. From these results, it can be observed that there is no significant loss of caustic at 100psi. However, this reduction levels should be checked at high pressures such as 200psi.

Table 4.2: Caustic Concentration (mol/L)

Runs	Volume of hemi caustic (mL)	Volume of acid (mL)	Acid Conc. (M)	Caustic Concentration of hemi caustic (M)
1 ^a	6.022	2.122	4.0	1.4095
2 ^b	6.0	2.122	4.0	1.4147
3 ^c	3.033	0.7550	4.0	0.9950
4 ^d	3.0	0.7440	4.0	0.9920

^a Feed; ^b Feed

^c Filtrate at 100psi; ^d Filtrate at 100psi

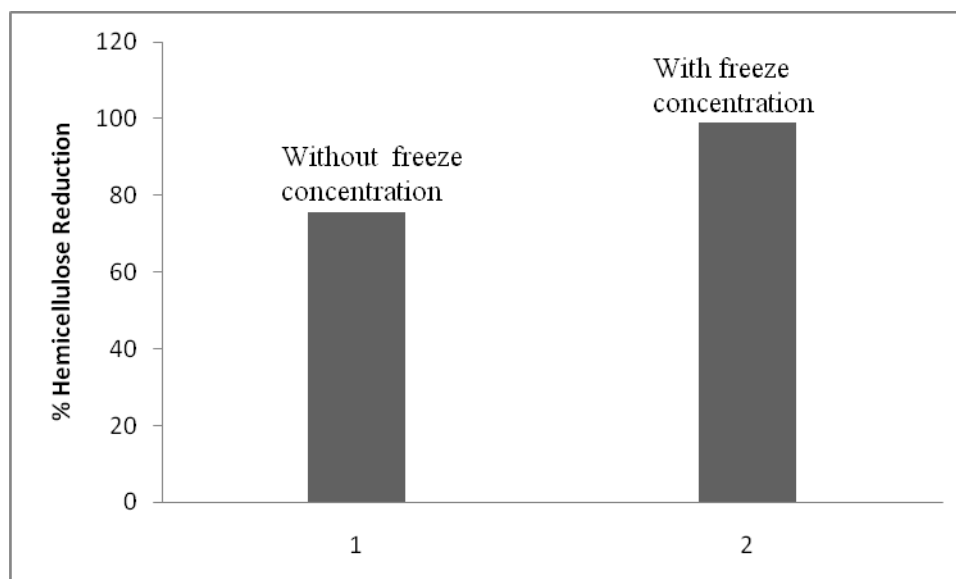


Fig. 4.2: % Hemicellulose reduction with and without freeze concentration at 150psi

Using regular acid hydrolysis procedure, Hemi cellulose content of permeate was measured for the cases of with and without freeze concentration at 150psi pressure was shown in Fig4.2. It was observed that the pretreatment has no effect at low pressures such as 100psi and high pressures such as 200psi. However, pretreatment has its effect at medium pressures such as 150psi.

4.1.2.1 Effect of Heat Treatment on Membrane Separation

To establish the fact that high temperature is not a suitable condition for membrane separation heat treatment was applied to hemi caustic stream and then subjected to membrane separation. Because, high temperature breaks down the long chains of hemi cellulose into shorter chains. The shorter chains easily move through the membrane, and would not separate efficiently. The following procedure was adopted for the combination of heat treatment and membrane separation experiment.

1. Heat the sample in a beaker on a hot plate
2. Load separator with heated sample
3. Heat separator wall with thermal cloth.
4. Push the solution through membrane by pressurizing with Nitrogen
5. Calculate wall temperature to be maintained to maintain sample temperature at the desired value.
6. Maintain wall temperature manually by measuring the wall temperature with a K type thermo couple and by supplying heat with thermal cloth
7. Collect permeate

Hemi caustic stream was subjected to membrane separation treatment at three different temperatures 50⁰C, 70⁰C and 90⁰C and at three different pressures 100, 150 and 200psi.

All samples were collected and hydrolyzed hemis content of the samples into sugars. These sugars were analyzed with HPLC. In the hydrolysis procedure, due to the presence of caustic, some of the Hydrochloric acid added for acid hydrolysis purpose reacted with caustic and formed salts which could be present in the solution in either soluble or insoluble form. Insoluble salts were filtered out. However, when more number of samples kept for HPLC analysis, dissoluble salts accumulated in the HPLC system and clogged the HPLC column. This bottleneck can be overcome by using a suitable HPLC column that could measure sugars content in basic environment. However, because of cost constraints this option was not attempted.

Instead of quantifying the performance of heat treatment, an attempt was made to qualify the same. Beckmann Coluter submicron particle analyzer which was shown in Fig 4.3 was used for this purpose. This instrument gives the mean particle size distribution (nm) of the particles present in solution. In addition to this, it also gives the results in the form of size distribution processor intensity, size distribution processor volume and size distribution processor number. Unimodal size distribution software was chosen to measure mean particle size of hemi caustic stream samples.

Throughout the size distribution analysis, it was assumed that caustic that was present in solution is in ionic or dissolved form and only particles that are present in solution are hemi cellulose.



Fig. 4.3 Beckmann Coluter submicron particle analyzer

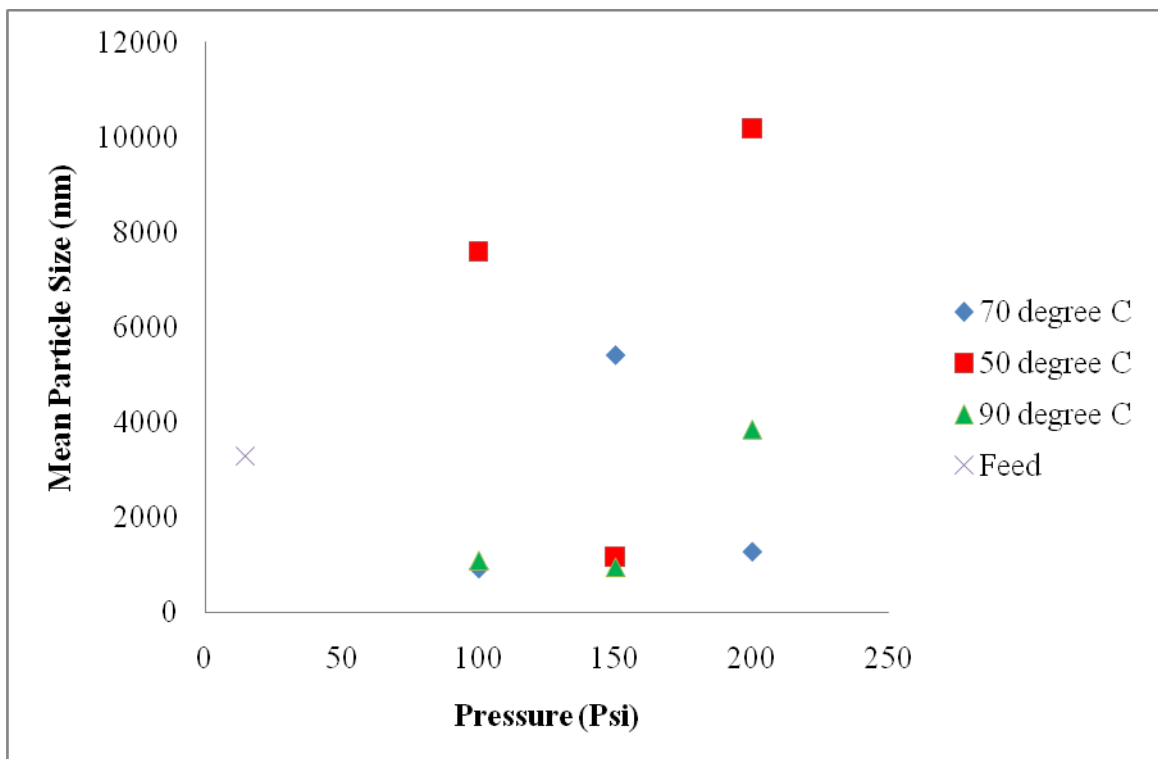


Figure 4.4: Effect of heat treatment on mean particle size at different temperatures and at different pressures (Analysis is made with acid hydrolysis)

Figure 4.4 shows the effect of heat treatment on membrane separation in terms of mean particle size. Higher reduction in mean particle size affects the performance of membrane separation negatively. With increase in temperature, particle size should get lower. It can be observed that except for 200psi pressure, mean particle size values for 90⁰C obeys this hypothesis. As heat treatment breaks longer chain hemi cellulose molecules into shorter chains, feed mean particle size should be greater than the mean particle size obtained at all higher temperatures than room temperature which is feed temperature.

Results presented in 4.4 obtained after subjecting the acid hydrolyzed samples to particle analyzer. This was done to know the effect of presence of salt particles in the hydrolyzed samples on mean particle size. The reason for these partially erratic results is due to the presence of salts in the hydrolyzed samples. 2hrs of heat treatment in the autoclave which is final part of the acid hydrolysis procedure might have broken down most of the hemi cellulose present in the feed sample. This could be the reason for less mean particle size of feed sample. After hydrolysis, all of the solid particles present in the sample may not be hemi cellulose. Some of them could be sugars and some of them could be hemis. Therefore, it can be concluded that the results presented in Figure 4.4 are preliminary results and may not completely represent the full picture of hemi cellulose chains in the samples.

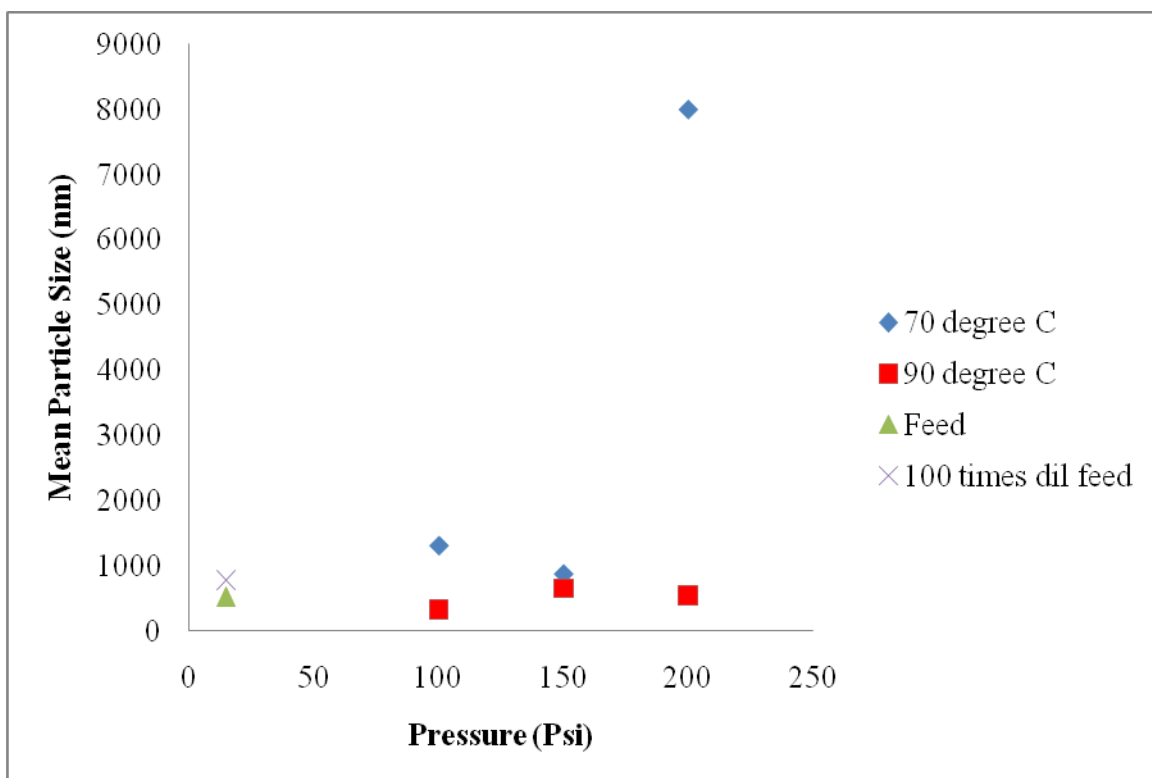


Figure 4.5: Effect of heat treatment on mean particle size at different temperatures and at different pressures (Analysis is made without acid hydrolysis)

Figure 4.5 shows the effect of heat treatment on membrane separation in terms of mean particle size. However, here collected samples were subjected to particle analyzer without acid hydrolysis. The results obtained in Figure 4.5 should be reliable results because these results are obtained without acid hydrolysis which means no extended heat treatment to destroy the hemi cellulose and no presence of salts to interfere with actual hemi cellulose mean particle size.

From the results presented in Figure 4.5, it can be observed that for 70⁰C temperature, with increase in pressure, there is a reduction in mean particle size except for 200psi pressure. However, for 90⁰C temperature, this trend was not observed. Mean particle size

increased from 100psi and 150psi and then dropped down at 200psi. However, mean particle size for 90⁰C is always lesser than 70⁰C which is the results of breaking down of hemi cellulose particles at higher temperature.

As far as the feed sample was concerned, it showed the same trend as was shown in Figure 4.4, feed sample result obtained with acid hydrolysis. Feed sample was diluted 100 times to study the effect of free Brownian motion of hemicelluloses particles on mean particle size. However, from the results shown in Figure 4.5, no significant effect was observed.

4.1.2.2 Effect of Freeze Concentration on Membrane Separation

Experiments were conducted to study the effect of freeze concentration on membrane separation. For the case of with freeze concentration, 50% of the water removed from hemi caustic and the resultant mother liquor was fed to the membrane separator. Effect was studied at three different pressures 100psi, 150 psi and 200psi. All experiments for the case of without freeze concentration were conducted at room temperature. Results were presented with and without hydrolyzing the filtrate samples for comparison purpose.

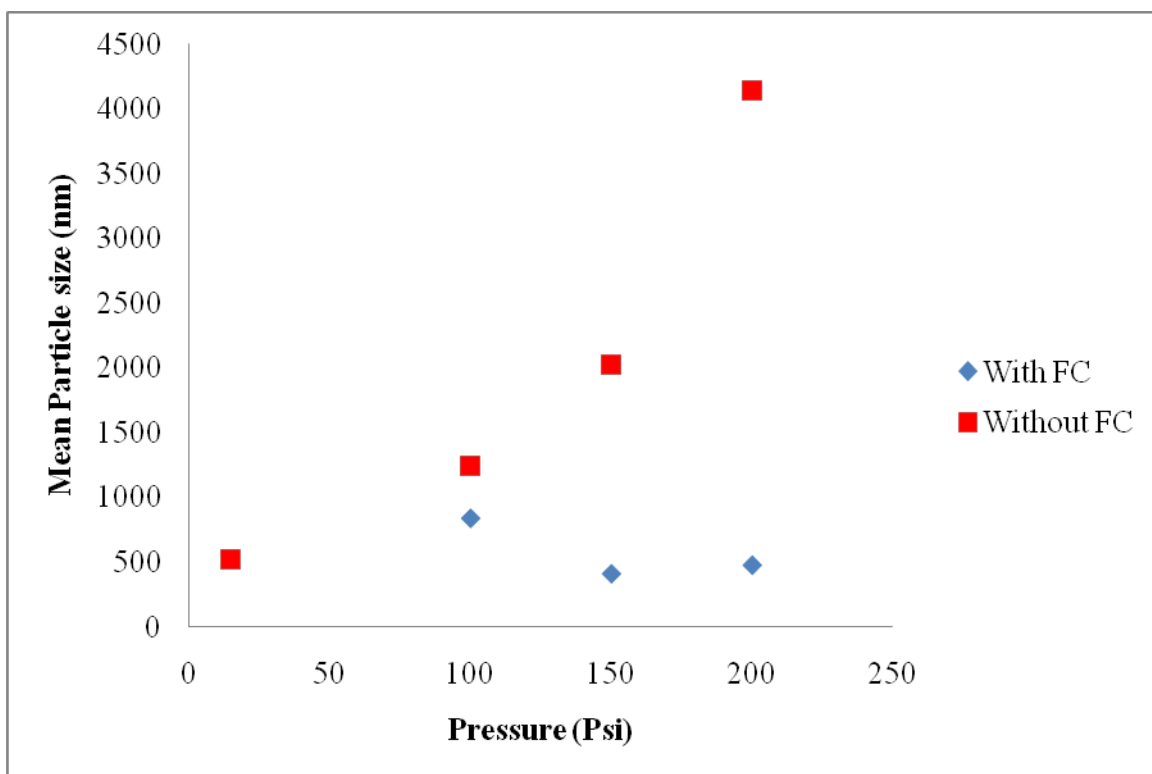


Figure 4.6: Effect of freeze concentration on mean particle size at different pressures

(Analysis was made without acid hydrolysis)

Figure 4.6 shows the effect of freeze concentration on membrane separation at different pressures in terms of mean particle size. Sample analysis was made without acid hydrolysis. It was observed that for the case of without freeze concentration, increase in operating pressure resulted in increase in mean particle size. This can be explained due to the effect of high pressure, longer chain hemi cellulose molecules were pushed through the membrane. However, similar trend was not produced for the case of without freeze concentration. Mean particle size for with freeze concentration should be more than without freeze concentration because of the tendency of formation of longer chain hemi cellulose molecules with decrease in temperature. However, graph shows the opposite trend. This could be due to blockage of membrane with longer chain molecules at low temperature and hence formed much smaller size hemi cellulose membrane over the

actual. As a result of this, only smaller particles could pass through the membrane and hence reduced the mean particle size for the case of with freeze concentration. In addition to this, it can be observed that difference in mean particle size for both the cases is increasing with increase in pressure.

Hemi cellulose is not agglomerating for the case of with freeze concentration on the membrane and hence, mean particle size is not going up with increase in pressure.

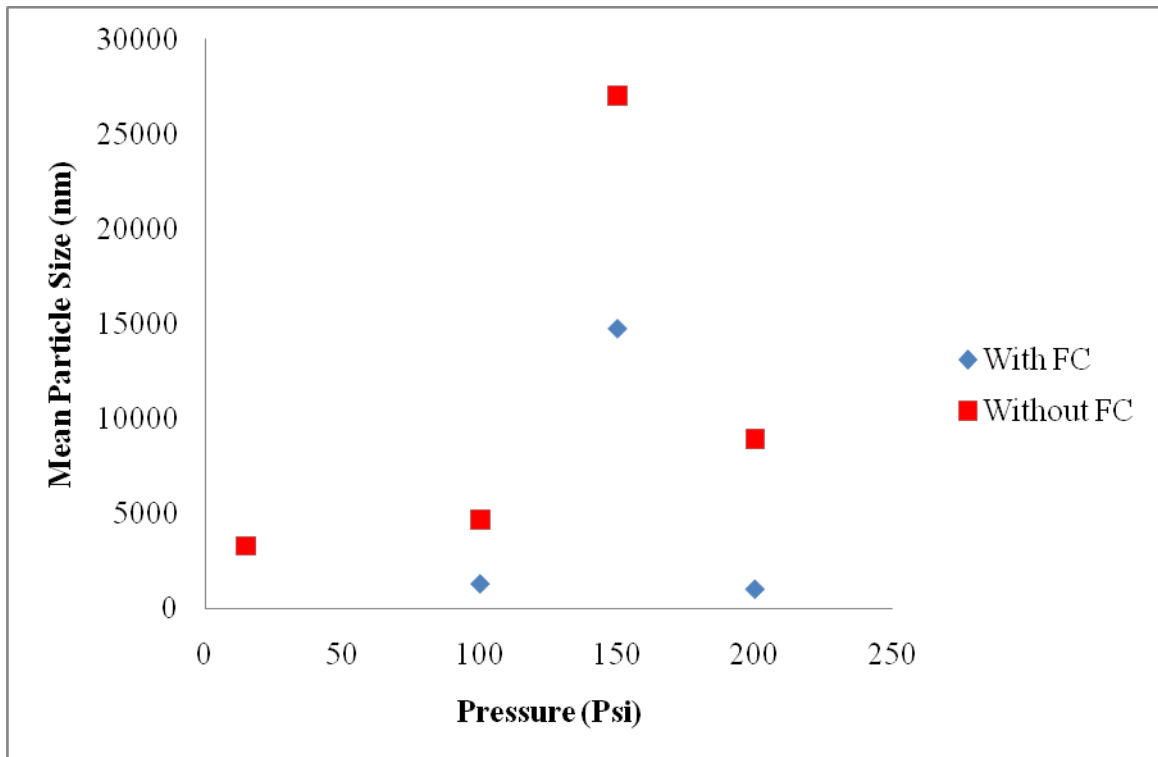


Figure 4.7: Effect of freeze concentration on mean particle size at different pressures

(Analysis is made with acid hydrolysis)

Similar trend was observed which was shown in Figure 4.7 when the analysis was done with acid hydrolysis except for 150psi pressure.

4.1.3 Gas hydrates

Though the freeze concentration is one of the promising methods either for separation of sodium ion from the hemi caustic extract or for increasing the concentration of hemi

cellulose to increase production of bioethanol, this method currently has a disadvantage. To get the caustic in pure form, ice crystals separated from the hemi caustic extract should be washed with process water, and this washing process causes the gradual reduction of the temperature of process water down to 0°C which in turn plugs the crystallizer tubes. Hence, it was proposed to study the gas hydrate separation technique which is similar to the freeze concentration technique, but gas hydrate separation can overcome the plugging problem because gas hydrates forms at 5°C . Long (2004), studied the separation of water from BCTMP mill effluent using gas hydrate separation technique, and they were successful in overcoming the plugging problem. Therefore, application of the same approach was proposed to observe the effect on the separation of sodium from hemi caustic extract and on increasing the concentration of hemi cellulose by freezing out the water from hemi caustic extract.

In this connection, an attempt was made to form gas hydrates with hemi caustic solution. Experimental setup for gas hydrate formation was shown in Figure 4.8. (Long and Hsieh 2004) reported that mixture of 85% CO_2 and 15% Isobutane forms gas hydrates at 4.4°C temperature and at 100psia pressure which is operable temperature and pressure under lab conditions. Therefore, the above mentioned gas mixture was used to form gas hydrates with hemi caustic solution. However, it formed CO_2 reacted with the caustic present in the hemi caustic solution and formed Sodium carbonate (white solution) as shown in Figure 4.9. Therefore, in view of losing caustic from hemi caustic solution, it was found that CO_2 and Isobutane gas mixtures is not suitable gas hydrate formation agent though its gas hydrate formation pressure is as low as 100psia. Therefore, it was proposed to use the mixture of Nitrogen and Isobutane to form gas hydrates without losing caustic present

in the hemi caustic solution as Nitrogen is an inert gas and it is not going to react with caustic present in the solution. However, gas hydrate formation pressure was not available in the literature for the above mentioned gas mixture. Thermodynamic calculations needed to be performed to evaluate the composition at which gas hydrate formation can be achieved with minimum operable pressure for the mixture of Nitrogen and Isobutane.



Figure 4.8; Experimental setup for the formation of Gas hydrates with hemi caustic solution



Figure 4.9: Hemi caustic solution before and after subjecting it to mixture of CO₂ and Isobutane

4.2 Treatment of Extractives of Brown Stock Filtrate

Extractives of brown stock filtrate were treated with dissolved air flotation. Original filtrate P^H was on base side which is named as base feed (BF). One experiment was conducted without changing P^H and another experiment was conducted after changing the P^H of the original filtrate towards acidic side (3.5)

Color, fines and extractives analysis was done three times for each collected sample and the results were averaged.

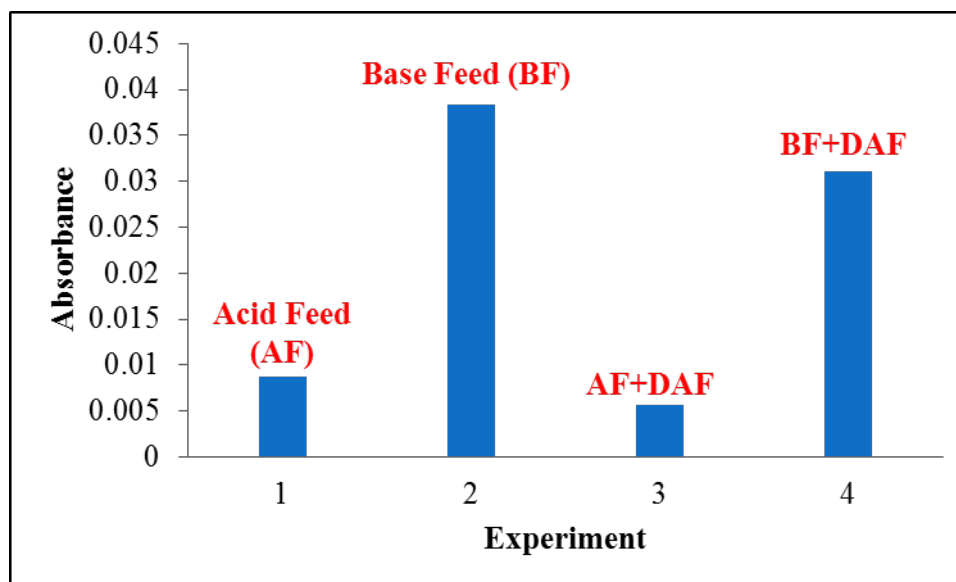


Figure 4.10: Color Absorbance comparison of brown stock filtrate after subjecting it to different experimental conditions (1 (Acidic feed); 2 (Basic feed); 3(Acidic feed after subjecting it to DAF); 4(Basic feed after subjecting it to DAF))



Figure 4.11: Appearance of brown stock filtrate after subjecting it to different experimental conditions (1 (Acidic feed); 2 (Basic feed); 3(Acidic feed after subjecting it to DAF); 4(Basic feed after subjecting it to DAF))

Figure 4.10 depicts the color comparison of the brown stock filtrate before and after subjecting it to DAF and polymer addition. Visual observation of Figure 4.11 was confirmed from the color absorbance results. It was observed that color of acidic feed

was much lesser than base feed. As far as acidic feed is concerned, DAF reduced color but not very significantly. Similar trend was observed in Base feed samples.

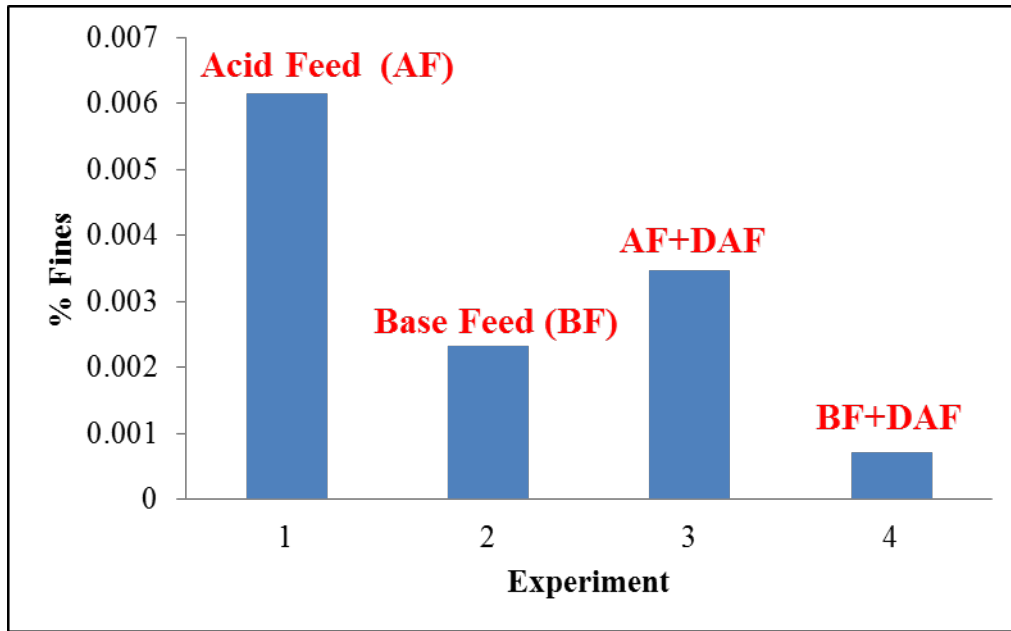


Figure 4.12: Fines comparison of brown stock filtrate after subjecting it to different experimental conditions (1 (Acidic feed); 2 (Basic feed); 3(Acidic feed after subjecting it to DAF); 4(Basic feed after subjecting it to DAF))

Figure 4.12 depicts the fines (total solids) comparison of the brown stock filtrate before and after subjecting it to DAF and polymer addition. DAF was equally successful in reducing fines by almost 50% both in acidic and basic environment. There should be a very less or no difference between fines values of acidic and basis environment as fines/solids do not have a tendency to react either in basic or acidic environment. However, here it is observed that fines in acidic feed are much higher than in base feed. The reason was attributed due to the manual collection of sample from the column and difference in level of agitation in the column at the time of sample collection.

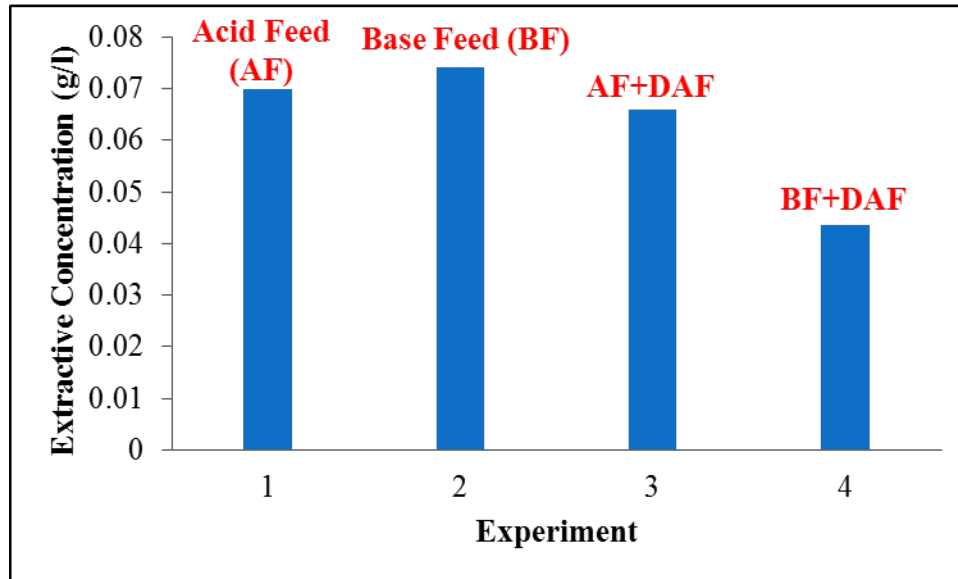


Figure 4.13: Extractives comparison of brown stock filtrate after subjecting it to different experimental conditions (1 (Acidic feed); 2 (Basic feed); 3(Acidic feed after subjecting it to DAF); 4(Basic feed after subjecting it to DAF))

Figure 4.13 depicts the extractives comparison of the brown stock filtrate before and after subjecting it to DAF. In this case, concentration of extractives for base feed is higher than the acidic feed. In case of acidic feed, DAF reduced the extractives concentration not very significantly.

In case of base feed, application of DAF operation reduced extractives more than in case of acidic environment. Extractives collected from the base feed sample can be seen in Figure 4.14.



Figure 4.14: Extractives collected from the base feed sample

4.2.1 Improved extractives measurement method

From many measurement trails, it was observed that existing extractives measurement method is not giving consistent results. This method from now onwards will be termed as indirect method as it will not give the accurate content of extractives on component basis. Because of the disadvantage the indirect method and to get more accurate picture of extractives content of brown stock filtrate, literature survey was done to find out any methods are available to determine the extractives content of a process stream such as brown stock filtrate without interference of human. Many such methods were found in the literature to measure the extractives. For example, (Orsa and Holmbom 1994) developed a convenient method for the determination of wood extractives in papermaking process water and effluents. Their method comprises of centrifugation to remove fibers, fines and other non-colloidal particles from dissolved and colloidal substances, extraction with methyl tert butyl ether, silylation, gas chromatography to determine the amount of wood extractives. The extractives are analyzed by GC with

automatic on column injection of silylated samples on a short thin film capillary column, providing direct determination of free fatty and resin acids, sterols, steryl esters and triglycerides. It was found that this method was utilized by many researchers. Therefore, attempt was made to analyze the extractives using the method developed by (Orsa and Holmbom 1994). Later, it was found that the method was too cumbersome to determine the two main extractives of brown stock filtrate namely Oleic acid and abietic acid. Therefore, further literature survey was carried out to find a simple method. For instance, Eberhardt et al., (2007) studied analyzing ethanol soluble extractives in southern pine wood by low field proton NMR. For example, (Claassen, Haar et al. 2000) developed a method for the rapid analysis of wood extractives using high pressure liquid chromatography with evaporative light scattering detection. All of the above mentioned methods gives exact results but they are time consuming and expensive.

Though extractive analysis using GC MS equipment is a robust method, it is time consuming as it involves many time delaying steps such as derivitization. Also, it needs more expertise to operate GC MS equipment. Therefore, it was decided to improve the existing indirect method such that it would give results that are as reliable as GC MS equipment results.

The main idea is to run indirect method with different solvents and one run of extractive measurement of brown stock filtrate with GC MS equipment. Then whichever solvent that gives the nearest result to GC MS result will be chosen as right solvent for the indirect method and continue measuring extractives with that solvent. One shot extractives measurement run with GC MS was discussed in Appendix.

Along with selection of right solvent for good extractive measurement procedure, some other changes were discussed in the following section by which the performance of indirect method could further be improved.

4.2.2 Improvements to Indirect method

The following changes were adopted to improve the existing indirect method.

Style of shaking: Vigorous mixing was essential for high extraction yields for lipophilic extractives. Evidently, strong mechanical action is required to obtain sufficient contact between lipophilic droplets and solvent droplets. In addition to this, mechanical shaking helps us to achieve good reproducibility. Therefore, hand shaking step of indirect method was replaced with mechanical shaking.

P^H adjustment: Literature survey was done to determine the P^H value at which maximum amount of extractives could be recovered into the solvent for measurement purpose. Strom (2000) mentioned that due to the high pH of the process water (10.6), resin acids and fatty acids would be dissolved to a high extent. Brown stock filtrate P^H value is on basic side. Therefore, it was decided to bring the value towards acidic side. (Orsa and Holmbom 1994) measured extractives of TMP water with GC MS equipment at different P^H values and confirmed that P^H 3.5 is the optimum value at which maximum extractives could be recovered. (Table4.3). Therefore, P^H value 3.5 was selected as improved condition for the existing indirect method.

Table 4.3: Amount of various component groups obtained by extraction of TMP water at different pH levels (Orsa and Holmbom 1994)

Extractives	pH= 3.5	pH= 6.5	pH= 8
Fatty resin acids (mg/l)	9.5	10	9.5
Sterols (mg/l)	2.4	2.2	2.2
Steryl esters (mg/l)	11.2	10.1	7.4
Triglycerides (mg/l)	21.4	20	13.5
Total	44.5	42.3	32.6

Extraction solvent: Selection of solvent place a vital role in recovering maximum possible extractives from the process stream. Indirect method uses di chloro methane as extractive solvent. However, according to (Orsa and Holmbom 1994), hexane-acetone mixture is the best solvent which extracts lipophilic extractives such as oleic acid and abietic acid. To confirm this fact for measurement extractives of brown stock filtrate, extractives of brown stock filtrate was measured with three different solvents such as Dichloro methane, Methyl Tert Butyl Ether and hexane-acetone mixture. All solvents used are HPLC grade except hexane and acetone.

Before approaching for solvent comparison trial, another set of experiments was conducted to determine the optimum ratio of hexane acetone mixture at which maximum extractives recovery could be possible.

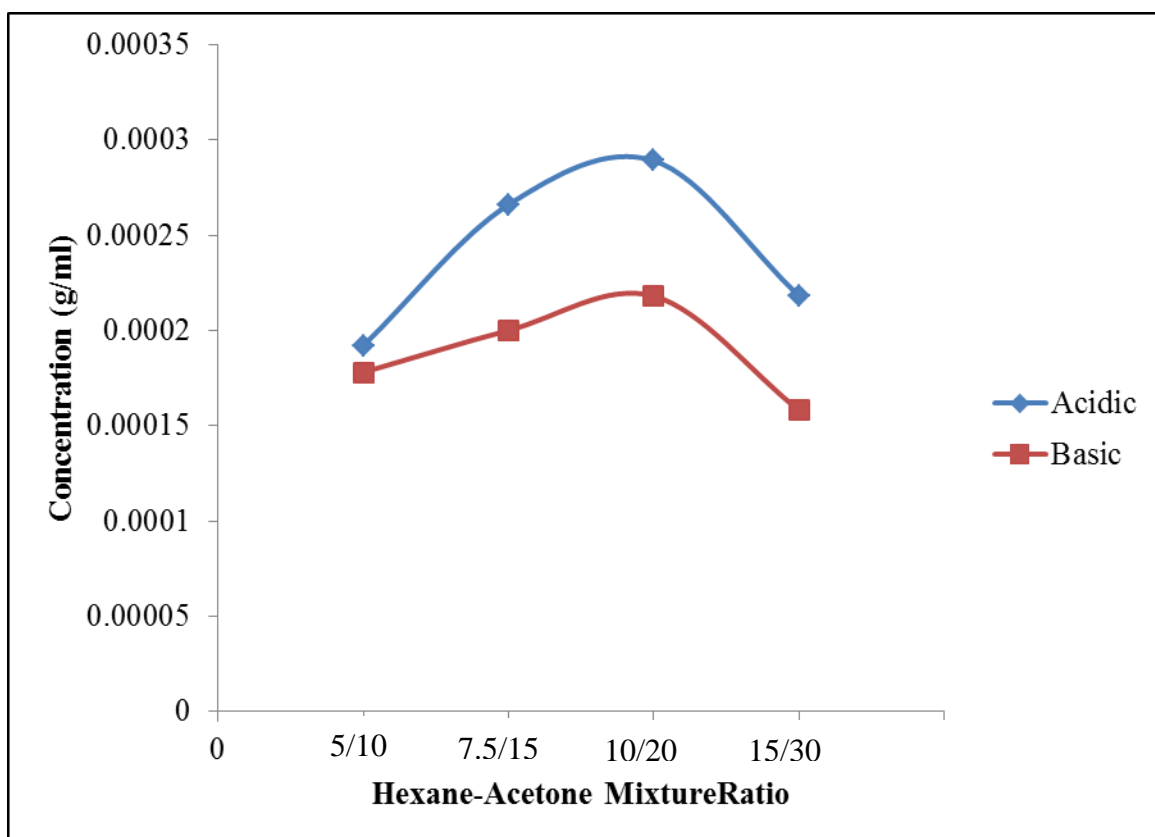


Figure 4.15: Variation of extractive concentration of brown stock filtrate (g/ml) with different hexane – acetone mixture ratios. (Basic sample refers to the original brown stock filtrate. Acidic sample refers to the P^H adjusted original brown stock filtrate at 3.5) From Figure 4.15, it can be observed that optimum hexane-acetone mixture ratio for maximum possible amount of extractives recovery is 10/20. Moreover, it can be observed that acidic P^H condition is favorable condition for extractive recovery when compared to basic P^H condition.

After obtaining above mentioned ratio, solvent comparison trail was conducted and result was shown in Figure 4.16.

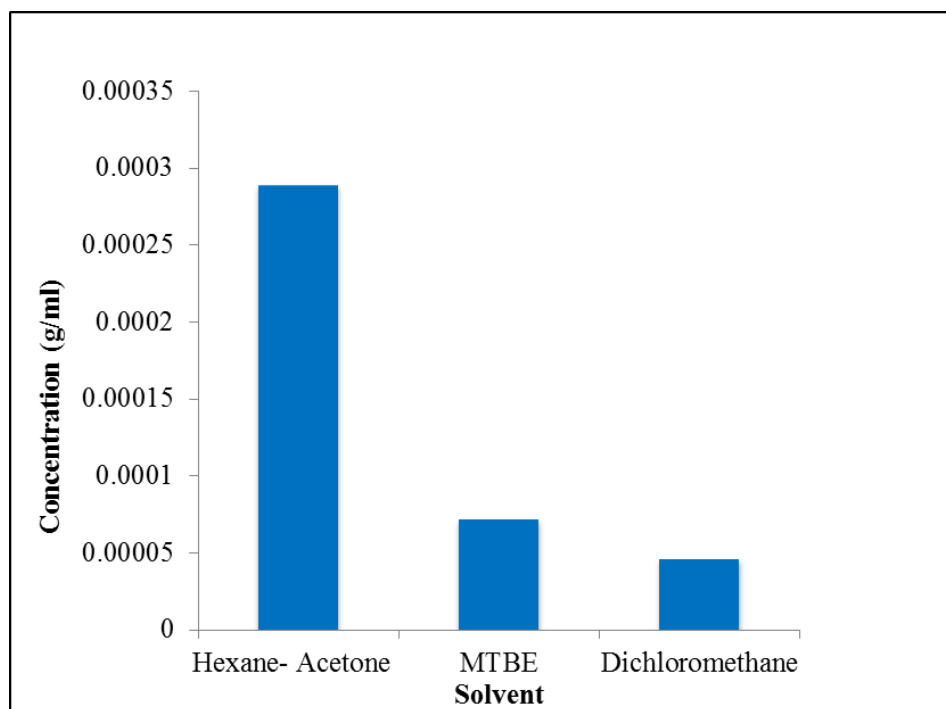


Figure 4.16: Variation of extractive concentration of brown stock filtrate (g/ml) with different solvents (Hexane-Acetone mixture ratio is 10/20)

It can be concluded from Figure 4.16 is that the Hexane and acetone mixture is the best solvent for the recovery of extractives from brown stock filtrate for measurement purpose as confirmed by (Orsa and Holmbom 1994)

4.2.3 Experiments with model compound

In view of running out of brown stock sample, it was decided to continue the DAF experiments and improvement of extractive measurement with model compounds. Initially Oleic acid and phenol was selected for this purpose as these are the compounds that were suspected to be the major compounds in the extractives.

An effort was made to improve reliability of indirect method by dissolving known concentration of model compound in water and the concentration was measured by indirect method.

0.2 g/l Oleic acid solution was prepared and Oleic acid content was measured using indirect method for two different shaking times 15 minutes and 30 minutes. Oleic acid content measurement was differed from existing measurement procedure in one aspect. Since, Oleic acid boiling point is 360°C , the organic layer was evaporated inside the oven at 105°C instead of using butchi rotavapor. Run 1 indicates 1hr drying time in the oven and run 2 indicates overnight drying time in the oven. Results presented in Figure 4.17 shows that excessive shaking time reduces the extracted Oleic acid concentration. In addition to this, it was observed that additional drying time decreases the extracted oleic concentration which is not a favorable condition to improve the quality of the extractive measurement procedure.

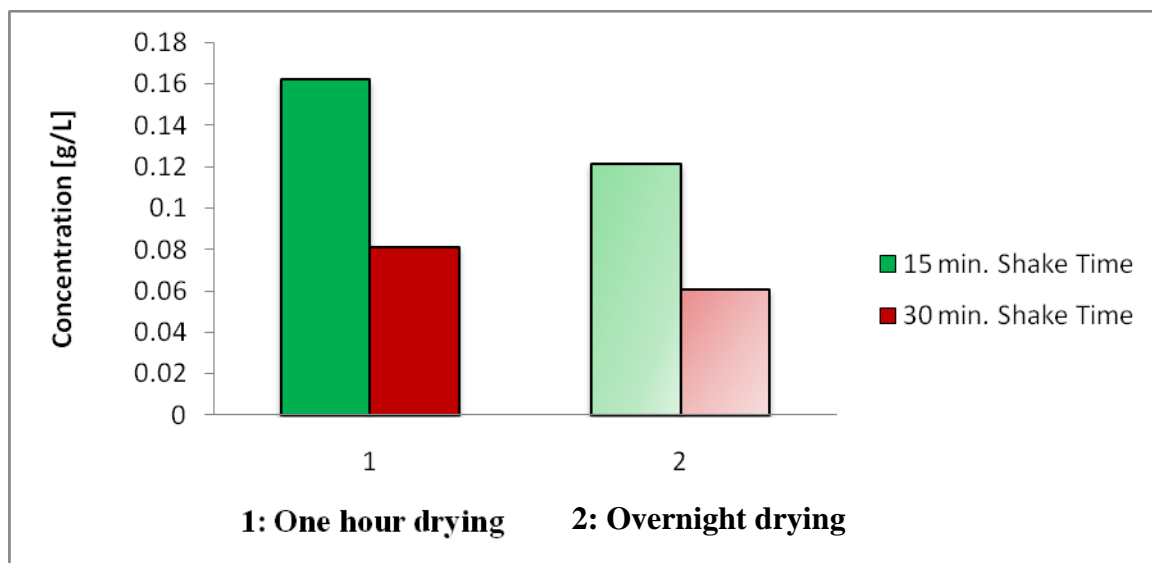


Figure 4.17: Variation of Concentration of measured Oleic acid (0.2g/l) Vs drying time at different shaking times

Another model compound, phenol was used to improve the extractive measurement procedure. Two different concentrations of phenol solution were prepared 30g/l and 60g/l and subjected to indirect method. 30 min shaking time and 1hr drying time of organic

layer in the oven at 105⁰C was employed. Result was shown in Figure 4.18. Extracted phenol concentration for two different initial concentrations is not as significant as extracted oleic acid concentration. This could be due to good amount of solubility of phenol (0.8g/l) in water and formation of hydrogen bonding with water molecules; it would have become difficult for the organic solvent to extract the phenol compound. Hence, it may be concluded that phenol cannot be a good model compound for extractives measurement procedure when compared to Oleic acid.

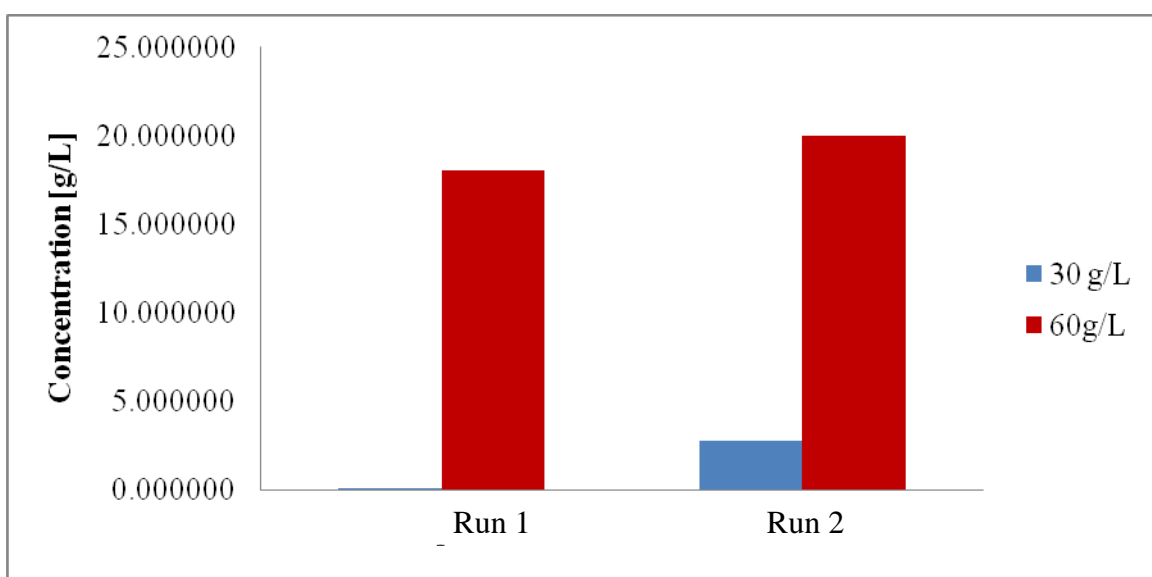


Figure 4.18: Phenol concentration measured by indirect method for two different initial concentrations

4.2.4 Estimation of Equilibrium Extractive Concentration of Brown Stock Filtrate

It may be possible to estimate the equilibrium extractive concentration of brown stock filtrate that is needed to maintain to recirculate the brown stock filtrate without facing the problem of extractives build up. Literature survey was done and relevant information was found in this connection.

For example, (Gilbert and Hsieh 2000) studied the effect of different detrimental substances which often buildup in the white water systems such as calcium, sodium, lignin, xylan, pH and fines on the physical properties (burst strength, ring crush, and z-directional tensile strength) of linerboard. The extent of accumulation in a closed mill are observed if extractives behave in a similar manner to the substances mentioned in (Gilbert and Hsieh 2000) paper. Effect of different detrimental substances present in brown stock filtrate including extractives on pulp properties needed to be experimentally determined. Once, this was achieved, experiments may be designed to predict the equilibrium concentration of extractives that is to be maintained in the brown stock filtrate to determine the extent of mill closure at which extractives buildup problem could be leveled off. A second relevant article was found in the literature.

For instance, (Xu and Deng 2004) developed a model to predict the buildup of dissolved solids when white water system of a paper machine was subjected to different degrees of closure. According to their model, the dissolved solids entering into the system from different water sources will not buildup endlessly, no matter how many times they are recycled and how tightly the system is closed. In addition to this, they proved that the final equilibrium concentration of any dissolved solids will be less than the flow proportional average concentration of that species in all outside water resources entering the system. Their laboratory results were in fair agreement with their model predictions.

Estimation of equilibrium concentration of extractives based on the above mentioned total dissolved solids model can be given as 550mg/l for 93% mill closure, assuming extractives behave in the same as total dissolved solids (sodium ion). Experiments needed to be conducted to prove the above mentioned estimate.

CHAPTER 5

CONCLUSIONS & FUTURE WORK

5.1 Treatment of Hemi caustic stream

5.1.1 Conclusions

It can be concluded that

- The freeze concentration method is capable of concentrating hemi caustic, but the ice that forms also contains some solid. A separation is apparent. A series of freezing steps, washing steps, or a combination may be used to reduce the amount of solid found in the frozen water.
- Pretreatment of hemi caustic with freeze concentration enhanced the membrane separation efficiency by 25% at 150psi and it has no effect on membrane separation at low pressures 100psi and high pressures 200psi.
- From the results of the acid hydrolysis, it was concluded that the presence of caustic does not destroy all the hemi cellulose present in the stream. This hemi cellulose was hydrolyzed into C5 and C6 sugars and it was found that the dominant sugar was xylose, a C5 sugar. However, C6 sugars are most conducive sugars for the production of bioethanol. A special type of bacteria could be used to generate bioethanol from C5 sugar produced.
- Heat treatment may not be a feasible method in the present case as applying heat breaks long chain hemi cellulose molecules into smaller molecules and escape through the membrane and ruin the whole purpose of separating out hemi cellulose from hemi caustic in the pursuit of recovering caustic.

- Effect of heat treatment and freeze concentration on membrane separation was studied and results were presented in terms of mean particle size using Beckmann sub-micron particle analyzer. High temperature produced low mean particle size particles and increase in pressure increased the mean particle size.
- Effect of acid hydrolysis on the quantification of hemi cellulose in terms of mean particle size was studied. Regular expected trends achieved in the analysis without acid hydrolysis was not correlated with the analysis was done with acid hydrolysis. This is due to the interference of salt particles that were formed during the acid hydrolysis pH adjustment step

5.1.2 Future work

Recommendations for future work are As follows

- (Schlesinger, Gotzinger et al. 2006) suggested a method to measure hemi cellulose content of hemi caustic stream using size exclusion chromatography. Because of cost constraints, this method was not applied. In future, this method could be used to qualify the effect of heat treatment and freeze concentration on membrane separation.
- On the other hand, suitable HPLC column that could measure the sugar content of hydrolyzed samples in basic condition can be purchased so that the quantification of the performance of membrane separation using acid hydrolysis could be achieved without clogging the HPLC equipment.
- Following 2 options to be studied to determine which option gives maximum cost and quality benefit.

- Option 1 (First step: freeze concentration – Second step: Membrane separation)
- Options 2 (First step: Membrane separation – Second step: freeze concentration)
- Gas hydrate technology was proposed as an alternative to freeze concentration method to circumvent the washing problem of ice crystals.
- Thermodynamic calculations needed to be performed to evaluate the composition at which gas hydrate formation can be achieved with minimum operable pressure for the mixture of Nitrogen and Isobutane.

5.2 Treatment of Extractive stream (Brown stock filtrate)

5.2.1 Conclusions

- Dissolved air flotation technique is capable of reducing color by 20%, fines by 80% and extractive contents of brown stock filtrate by 42% based on original feed condition. Indirect method (Dichloro methane solvent extraction) was used for extractives measurement in this case.
- Existing extractives measurement method was improved by the following means
 - Changing the style of shaking
 - Adjusting the P^H to 3.5
 - Choosing the right extractive solvent (Hexane-Acetone Mixture, Methyl Tert Butyl Ether)

- Solvent comparison experiments were conducted and results shown that Hexane-Acetone is the best solvent for extracting lipophilic extractives as confirmed by (Orsa and Holmbom 1994)
- Optimum ratio of Hexane-Acetone solvent mixture was found as 10/20 for extracting maximum possible amount of extractives from brown stock filtrate
- The following approach was suggested to estimate equilibrium extractive concentration of brown stock filtrate that is needed to maintain to recirculate the brown stock filtrate without facing the problem of extractives build up.
 - Study the effect of different detrimental substances presented in the brown stock filtrate on pulp properties. Experimental design for this section of work can be referenced from (Gilbert and Hsieh 2000)
 - Using the approach of (Xu and Deng 2004) , equilibrium concentration of extractives can be determined considering the effect of detrimental substances on brown stock filtrate which was not considered by (Xu and Deng 2004)
 - Estimation of equilibrium concentration of extractives based on the above mentioned total dissolved solids model was given as 550mg/l for 93% mill closure, assuming extractives behave in the same as total dissolved solids (sodium ion).

5.2.2 Future Work

Recommendations for future work are As follows

- Use CO₂ instead of air because it is more soluble in H₂O and has the possibility to increase extractives removed from brown stock filtrate.

- Continue to perform DAF tests with more accurate setup and with additives
- Perform tests to see how the additives affect process water.
- Research how the Rayonier pulp is effected by additives so that option of recycling DAF treated water with additives could be studied.
- Find out suitable coagulant that flocs fines and extractives at the same time do not disturb the pulp quality
- Alum could be added to coagulate color and to reduce the amount of polymer addition and study whether alum water effect the pulp quality or not.
- Studies needed to conduct to know how much %of the DAF treated brown stock could be recycled without facing the problem of accumulation of extractives. Literature survey was done in this connection. No article was found related to extractives build up in closed water systems of mill. However, (Xu and Deng 2004) have developed a model to predict the buildup of dissolved solids in a white water system when the system is closed to different degrees. Similar approach can be used to predict the equilibrium concentration of extractives at which the system could be run without facing the problem of extractives buildup.
- Experiments needed to prove the given estimate for equilibrium concentration of extractives without damaging the pulp or the level of accumulation could be reduced to level off the pulp property.

Appendix A

Table A.1: Figure 4.1 Data

Collection Time							
Collection	0	1	2	3	4	5	6
Time	1:00 PM	1:40 PM	2:10 PM	2:40 PM	3:10 PM	3:40 PM	4:10 PM
Elapsed Time [min]	0	40	70	100	130	160	190
TDS Mother Liquor							
Total Mass [g]	1008.9	-	-	-	-	-	209.2
Tray Mass [g]	2.2783	2.2858	2.2801	2.2742	2.232	2.2694	2.2832
Tray + Wet [g]	12.468	12.4991	12.5804	12.6829	12.5517	12.6925	12.7258
Location	1.1	1.2	2.1	2.3	3.2	2.4	4.1
Tray + Dry [g]	2.9921	3.0502	3.0624	3.2081	3.127	3.2777	3.3384
Mass of Water [g]	9.4759	9.4489	9.518	9.4748	9.4247	9.4148	9.3874
Mass of Solid [g]	0.7138	0.7644	0.7823	0.9339	0.895	1.0083	1.0552
TDS [%]	7.01	7.48	7.59	8.97	8.67	9.67	10.10
Collected Ice							
Mass of Beaker [g]	-	108.7	108.8	108.3	108.8	108.4	108.8
Beaker + Ice [g]	-	231.5	309	244.7	228	159.1	174.1
Mass of Ice [g]	-	122.8	200.2	136.4	119.2	50.7	65.3
TDS of Melted Ice							
Tray Mass [g]	-	2.2725	2.2632	2.2026	2.2526	2.2555	2.2886
Tray + Wet [g]	-	12.5031	12.4662	12.4788	12.5137	12.5387	12.5941
Location		1.3	2.2	3.1	3.3	3.4	4.2
Tray + Dry [g]	-	3.0283	2.9566	2.8779	2.9887	3.0241	3.0673
Mass of Water [g]	-	9.4748	9.5096	9.6009	9.525	9.5146	9.5268
Mass of Solid [g]	-	0.7558	0.6934	0.6753	0.7361	0.7686	0.7787
TDS [%]	-	7.39	6.80	6.57	7.17	7.47	7.56

Table A.2: Figure 4.2 Data (FC means Freeze Concentration)

Pressure	Without FC	% Reduction	With FC	% Reduction
14 psi	1.589	Feed	1.589	Feed
100 psi	0.096	93.96	0.088	94.46
150 psi	0.014	99.11	0.387	75.64
200 psi	0.286	82	0.292	81.62

Table A.3: Figure 4.4 to 4.7 Data

S.No	Experiment				Unimodal Mean size (nm)
1	With freeze concentration (100psi)				1293.5
2	With freeze concentration (150psi)				14727.8
3	With freeze concentration (200psi)				1012
4	Without freeze concentration (100psi)				4658.7
5	Without freeze concentration (150psi)				27029
6	Without freeze concentration (200psi)				8907.5
7	Mother Liquor from freeze concentration (Sample A)				1908.6
8	Mother Liquor from freeze concentration (Sample B)				4638.8
9	Mother Liquor from freeze concentration (Sample C)				1237.9
10	Water sample from freeze concentration (Sample A)				5978.7
11	Water sample from freeze concentration (Sample B)				2412.9
12	Water sample from freeze concentration (Sample C)				2881.6
13	T (50C) P(100 psi) without freeze concentration				7597.6
14	T (50C) P(150 psi) without freeze concentration				1160.6
15	T (50C) P(200 psi) without freeze concentration				10185.1
16	T (70C) P(100 psi) without freeze concentration				916
17	T (70C) P(150 psi) without freeze concentration				5423
18	T (70C) P(200 psi) without freeze concentration				1272.2
19	T (90C) P(100 psi) without freeze concentration				1097.8
20	T (90C) P(150 psi) without freeze concentration				957
21	T (90C) P(200 psi) without freeze concentration				3850.3
22	Feed sample A	Unclear			3291.2
23	Feed sample B	Unclear			4144.9
24	Water sample A	Unclear			1094.2
25	Water sample B	Unclear			2808.6
26	Feed sample A without acid hydrolysis				5766.5
27	Feed sample B without acid hydrolysis				3121.9
28	Feed sample C without acid hydrolysis				490.5
29	Feed				528.1

Table A.4: Figure 4.10 Data

Experiment	Color Absorbance
Acid Feed	0.008666667
Base Feed	0.038333333
Acid Feed+DAF	0.005666667
Base Feed+DAF	0.031

Table A.5: Figure 4.12 Data

Experiment	% Fines
Acid Feed	0.006146
Base Feed	0.002326
Acid Feed+DAF	0.003466
Base Feed+DAF	0.000705

Table A.6: Figure 4.13 Data

Experiment	Extractives content (g/l)
Acid Feed	0.069838
Base Feed	0.074224
Acid Feed+DAF	0.065789
Base Feed+DAF	0.043522

Table A.7: Figure 4.15 Data

Hexane-Acetone Mixture Ratio	Acidic	Basic
5/10	0.000192	0.000178
7.5/15	0.000266	0.0002
10/20	0.000289	0.000218
15/30	0.000218	0.000158

Table A.8: Figure 4.16 Data

Solvent	Extractive concentration (g/l)
Hexane- Acetone	0.000289
MTBE	0.000072
Dichloromethane	0.000046

Table A.9: Figure 4.17 Data

Test	Shake time	Dry vial	Vial+Dry sample	conc.	Drying Time
1	15	13.272	13.28	0.16	1 hour
1a	15	13.272	13.278	0.12	overnight
2	30	13.291	13.295	0.08	1 hour
2a	30	13.291	13.294	0.06	overnight

Table A.10: Figure 4.18 Data

Initial concentration	Extracted phenol concentration (g/l)	
	Run 1	Run 2
30g/l	0.1	2.5
60g/l	18	20

Appendix B

As mentioned in result and discussion section, improvement of indirect method approach needs a one shot estimate of extractives in brown stock filtrate using GC MS equipment. GC MS procedure itself needs a rough estimate to start with. This estimate tells us in what range standards are needed to be prepared to develop a standard curve for the extractives measurement. Standard curve is the plot between different signals for different known concentrations of standards (Oleic acid and Abietic acid which are prominent extractives present in the brown stock filtrate). This will help us to know the concentration of actual brown stock from the signal obtained when it is subjected to GC MS equipment. Literature survey needed to be done to know the rough estimate of extractives present in the liquid similar to brown stock filtrate.

GC MS – Spectra Analysis involves 2 steps namely derivitization of the sample and subjecting derivitized samples to GC MS equipment under recommended conditions.

Table A.1 shows the chemicals used for the derivitization of brown stock filtrate sample.

Table A.2 shows the chemicals used for the preparation of standards

Table B.1: Derivitization chemicals

Chemicals	Purpose
0.05M Sulphuric acid	P ^H adjustment
Bromocresol green	P ^H Indicator
MTBE Solvent	To dissolve extractives
Trimethylchlorosilane (TMCS)	Derivitization
N,O-Trimethylsilyl-trifluoro acetamide (BSTFA)	Derivitization

Table B.2: Standard Chemicals

Standard Chemicals	Internal Standard Solution (0.02 g/l)	External Standard Solution (0.2 g/l)
Heneicosanoic acid	Purpose: accompanies the sample when the sample is being tested in GC	Purpose: To compare sample peaks
Betulinol		
Cholesteryl Heptadecanoate		
1,3 dipalmitoyl-2-oleoyl-glycerol		
MTBE Solvent		

Sample Preparation and Derivatization steps can be summarized as follows.

1. Heating of the Sample container at 60⁰C
2. PH adjustment to 3 with Sulfuric acid and bromocresol green
3. Addition of Internal standard solution and centrifugation
4. Repetition of extraction and centrifugation twice with MTBE solvent
5. Combine MTBE Phases from all extractions and dry them over silica gel
6. Combine MTBE Phases from all extractions and dry them over silica gel
7. Evaporate the solvent
8. Add BSTFA and TMCS to derivitize the sample

The following conditions were used for GC MS Analysis

- Column: 100% dimethyl polysiloxane, length 6m-8m, i.d. 0.53mm, 0.15 micrometer phase thickness
- Temperature Program: 100⁰C in 1.5min, 12 ⁰C/min >=340⁰C in 5 min
- Temperature programmable injector: “On column” type
- Injector volume: 0.4 micro liter
- Detector type: FID, at 340⁰C

Results and Findings from the first authentic trial

- External Standard sample solution peaks were analyzed. All standard chemicals were absent except heneicosanoic acid.
 - Chemical might be absent in the sample
 - Chemical might not be gasified because of it's high boiling point
 - Chemical might not be included in GC MS Library

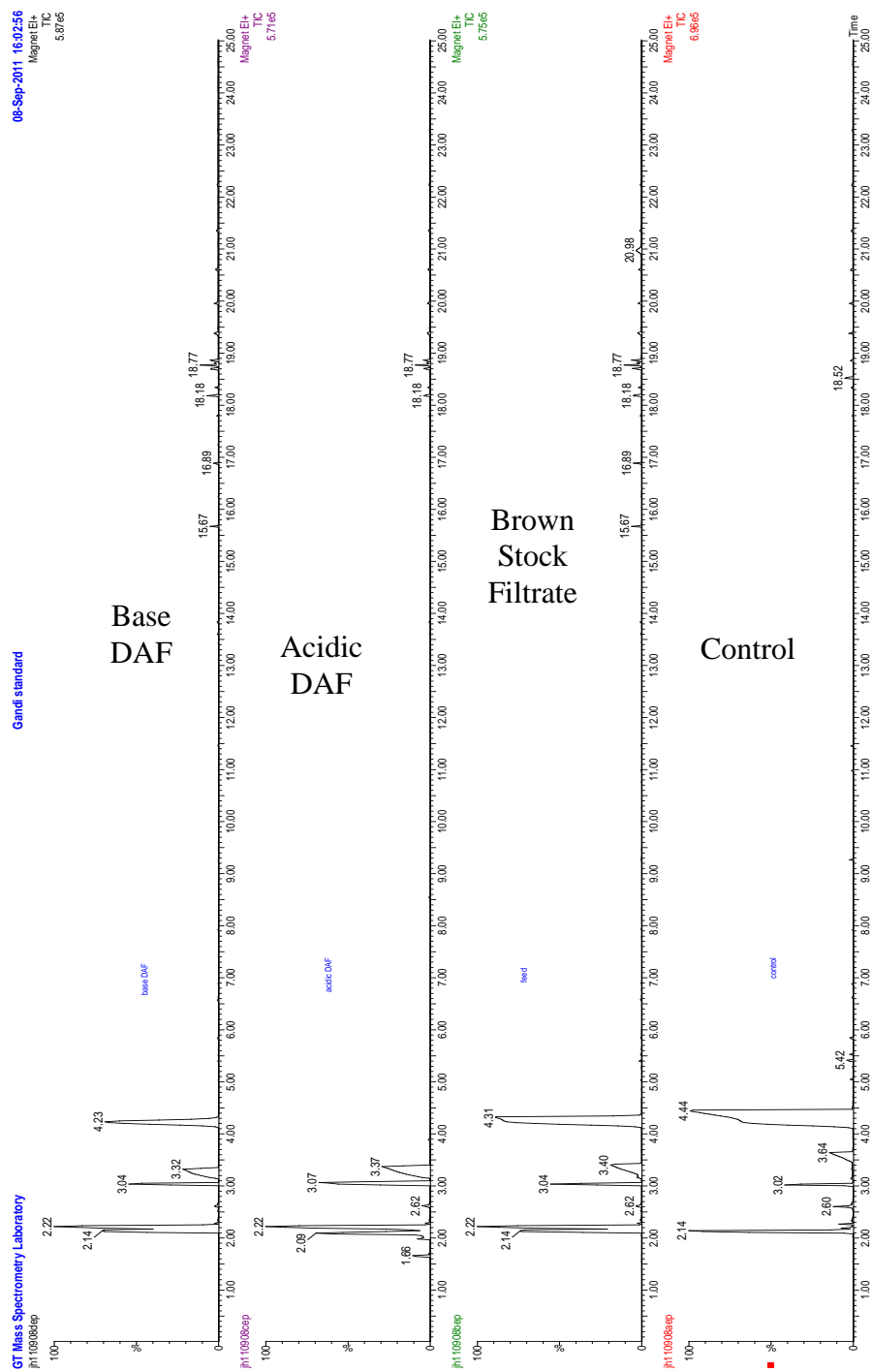


Figure B.1: GC MS Result 1

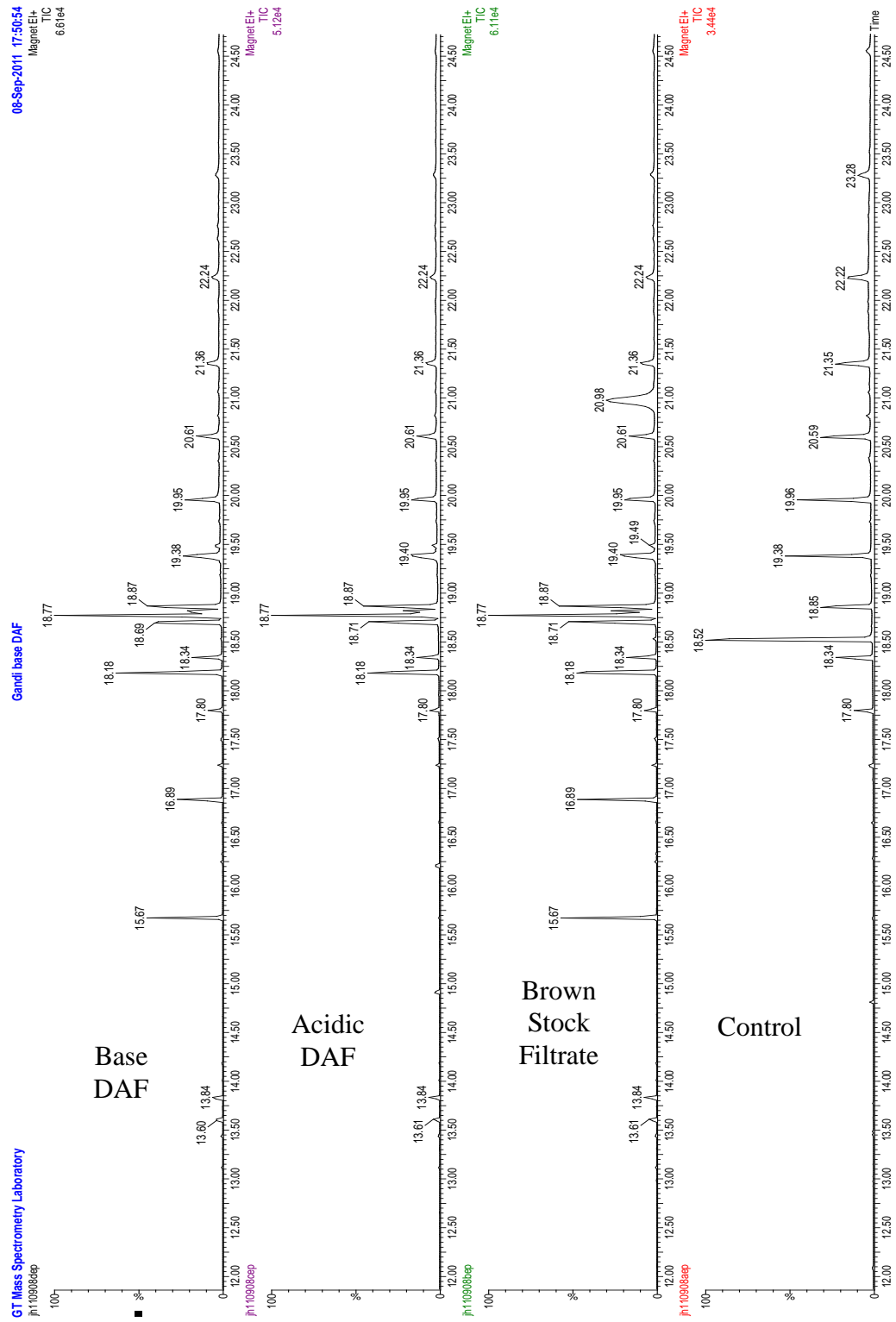


Figure B.2 GC MS Result 2

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